ABSTRACT

GROWTH AND TRANSPORT PROPERTIES OF Sb-DOPED ZnO NANO/MICROWIRES

by Nada Ali Masmali

In this research, the transport properties of Sb-doped ZnO wires were investigated. ZnO:Sb wires were grown successfully using a thermal evaporation method with about 9%-4% atomic of Antimony (Sb) and with diameters ranging from 1.5µm to 20 µm. nano-wires with diameters less than 50nm were also grown when slowing down the cooling process in a controlled way. The charge carriers of the ZnO:Sb wires were found to be free electrons using the hot probe measurement. In-situ annealing in air was used to activate the dopants of Sb in ZnO wires and to attempt to change the conductivity type from n-type to p-type. The most promising strategy for getting p-type doping is annealing ZnO:Sb wires at 150 °C in the dark. Annealing and then cooling slowly to room extends the time duration of the persistent photoconductivity.
GROWTH AND TRANSPORT PROPERTIES OF Sb-DOPED ZnO NANO/MICROWIRES

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Chapter 1

Introduction

1.1 Background

Zinc Oxide is a group II-VI semiconductor that attracted attention in materials science since 1935.\textsuperscript{1,2} The first successful industry of Zinc Oxide was in 1840 using the “French process”, in which Zinc burns in air.\textsuperscript{3} In 1852, The New Jersey Zinc Company developed a new manufacturing technique to produce Zinc Oxide by melting pure Zinc with coal, and this came to be known as the “American process”.\textsuperscript{3} Both the French and the American processes are considered as primary methods to prepare ZnO. In Zinc Oxide, there is an ionic bonding between a Zinc atom, which has two electrons in the outer shell, and an Oxygen atom with six electrons in the valence shell. Therefore, the Zinc loses its outer electrons and becomes positively charged (Zn\textsuperscript{++}) to give them to Oxygen, which becomes negatively charged (O\textsuperscript{--}). ZnO crystal has the wurtzite structure, which has a hexagonal symmetry as illustrated in Figure 1.1. However, under high pressure, the ZnO crystal exhibits a rock salt phase that has a cubic symmetry.\textsuperscript{1,2,3,4,5} Zinc Oxide has a wide band gap of 3.37 eV and a large, free exciton binding energy of about 60 meV at room temperature. Moreover, ZnO is characterized by high thermal conductivity, high transparency, high electron mobility and large piezoelectric constants.\textsuperscript{6,7} Therefore, these unique characteristics make Zinc Oxide useful in a variety of applications. ZnO nanostructures are beneficial in applications such as UV light emitting diodes, biological, and gas and chemical sensors. Moreover, Zinc Oxide single crystals are promising in the development of optoelectronic,
spintronic and piezoelectric devices.  

![Figure 1.1: The wurtzite structure of ZnO crystal.](image)

1.2 Doping

The majority of charge carriers in undoped ZnO are free electrons. Therefore, being an n-type semiconductor is considered a limitation of using ZnO in electronic devices such as UV-LED and solar cells. However, doping ZnO with metal or semimetal elements would improve its efficiency whether by producing p-type conductivity or by enhancing the properties of ZnO in general and its electrical properties in particular. Zn atoms are substituted by group III elements such as Al, Ga, or In to obtain n-type doping in ZnO. Replacing O atoms with group VII such as Cl or I, is another method to obtain n-type conductivity in ZnO. Although achieving p-type doped ZnO has been a difficult task, p-type doping could likely be satisfied by substituting group I elements such as Li, Na, or K. Also, p-type doping could be achieved using group V elements such as N, P, or Sb.

1.3 Literature Review

Producing p-type doped ZnO proved to be a difficult task. Thus, achieving the p-
type conductivity in ZnO attracts significant research interest. Doping with semimetals is a reasonable approach to controlling the conductivity type. Considerable research efforts focused on Antimony, which is a group V element, as one of the outstanding candidates. Different research groups have reported p-type behavior in Sb-doped ZnO.\textsuperscript{12, 13, 14} According to Hall effect measurements, the electron mobility of Sb-doped ZnO thin films is higher than the electron mobility of undoped ZnO thin films.\textsuperscript{15} A Seebeck coefficient of -0.35 mV/K has reported for individual Sb-doped ZnO micro/nanobelts using thermoelectric effect measurements.\textsuperscript{16} H. Liu, et al. observed n-type conductivity of ZnO:Sb with electron concentrations between $10^{16} - 10^{20}$ cm\textsuperscript{-3} in ZnO:Sb layers using the Hall effect measurement.\textsuperscript{17} C. Lee, et al. claimed that the majority charge carriers of ZnO nanowires are electrons, when they investigated the impact of the temperature dependent thermoelectric power of single nanowires.\textsuperscript{18} Nanowires are good one-dimensional systems in determining the transport properties and they have a large surface to volume ratio.\textsuperscript{4}

Thermal annealing is used to enhance the structure of ZnO and its electrical properties under different conditions. The annealing influence on the electrical properties has been studied on Sb-doped ZnO thin films, and an increase in the electron concentration was reported.\textsuperscript{17} According to C. Swartz, a conducting sheet will be generated on the surface of ZnO under thermal annealing treatment with a temperature higher than 227 °C.\textsuperscript{19} Exposing ZnO single crystals to light influences its electrical properties and a massive decrease in the resistance has been reported at room temperature.\textsuperscript{20} The photo resistance effect in ZnO single crystals takes time to vanish after turning the visible light or UV illumination off and leaving the crystal in the darkness, which leads to the persistent photoconductivity phenomenon.\textsuperscript{21}


1.4 Motivation

The effect of doping ZnO with Sb and investigating the type of conductivity are important contemporary topics to investigate, so they catch the attention of many researchers. The aim of this thesis is to investigate the electric transport properties of Sb-doped ZnO nano and microwires. Also, the low-temperature in-situ annealing effect on the electrical properties will be studied in this research, as well as the photoconductivity under the visible illumination and the persistent photoconductivity. Finally, thesis will outline our efforts to improve the synthesis techniques for growing improved ZnO:Sb nanowires.

In chapter two of this thesis, the theory of conductivity type measurement will be discussed, and the basics of thermal annealing effect. Also, the phenomenon of persistent photoconductivity will be addressed. Chapter three will discuss the experimental techniques including the sample fabrication, thermoelectric effect measurement, and the low-temperature in-situ annealing effects setup. Additionally, SEM images and EDX analysis will be shown. In chapter four, the results of the electrical properties measurements will be analyzed, and the main observations will be highlighted. In chapter five, a brief conclusion will be drawn. In chapter six, further potential studies will discuss.
Chapter 2

Theory

2.1 Conductivity Type of ZnO

The properties of semiconductors depend directly on the concentration and the type of the charge carriers. That explains the importance of determining the conductivity type of the semiconductor to understand the full picture of its transport properties. In n-type semiconductors, the Fermi level is close to the conduction band as is illustrated in Figure 2.1(a). On the other hand, the Fermi level is close to the valence band in p-type semiconductors as is shown in Figure 2.1(b).

Figure 2.1: A schematic diagram of Fermi level and the bands of semiconductors (a) an n-type semiconductor, and (b) a p-type semiconductor.
2.1.1 Hall Effect

The most common technique to differentiate whether the semiconductor is p-type or n-type is the Hall Effect measurement. When a semiconductor with a flowing current is placed in a magnetic field that is perpendicular to the current direction, the charge carriers are deflected to each side of the semiconductor as indicated in Figure 2.2. As a consequence, a potential difference will be generated, which is known as Hall voltage \( V_{H} \) and given by:

\[
V_{H} = \frac{RB}{W}.
\]

Where: R is the Hall coefficient, B the magnetic field, W the thickness of the sample, and I the flowing current. Depending on the sign of the Hall voltage \( V_{H} \) the type of conductivity is determined. So, if the \( V_{H} \) has a positive sign that means the majority charge carriers are p-type; otherwise, the semiconductor is n-type. In spite of the success of Hall measurements to determine the conductivity type and the charge concentration, it is clearly difficult to apply Hall effect on ZnO:Sb microwires.

![Figure 2.2: Schematic cartoon to represent the principle of Hall effect measurement of an n-type semiconductor.](image)
2.1.2 Thermoelectric Effect

The thermoelectric effect is another technique that allows investigating the conductivity type of semiconductors. This method depends on the Seebeck effect, which is given by:

\[ S = -\frac{\Delta V}{\Delta T}. \]

According to equation 2.2, applying a temperature gradient will produce a different voltage between the hot end and cold end. By measuring the generated voltage, the type of charge carriers will be determined. If a positive voltage is obtained when the hot source is placed on the positive probe that means the charge carriers are p-type as shown in Figure 2.3 (b). On the other hand, as is clearly described in Figure 2.3 (a), placing the hot source on the positive terminal of an n-type semiconductor will generate a negative voltage.

Figure 2.3: Schematic diagram to indicate the (a) thermoelectric effect in an n-type semiconductor, and (b) thermoelectric effect in a p-type semiconductor.
2.1.3 Field Effect Transistor

Metal Oxide Semiconductor Field Effect Transistor (MOSFET) is a preferable device to investigate the conductivity type of a semiconductor. The flow of current between the drain and source can be controlled by applying a voltage across the gate ($V_g$). The behavior of the drain-source current ($I_{ds}$) can then be used to determine the conductivity type of the semiconductor. For an n-type semiconductor, as the applied voltage across the gate increases the measured $I_{ds}$ will increase as well. However, in the p-type semiconductor when the gate voltage increases the measured $I_{ds}$ will decrease. Figures 2.4 (a) and (b) represent the electric circuit that can be used to determine the conductivity type of semiconductor (including the Potentiometer which allows applying different values of voltage across the gate) and the MOSFET device, respectively.

![Diagram](image)

Figure 2.4: (a) The electric circuit used to determine the conductivity type using different values of $V_g$, and (b) The back gate- MOS Field Effect Transistor with ZnO:Sb wire as semiconductor channel.
2.2 Effect of Annealing on The Electrical Properties of ZnO

When a semiconductor is thermally activated, its conductivity will increase. In the valence band, electrons will absorb energy, so if the energy is higher than the band gap energy that allows them to transfer to the conduction band leaving holes in the valence band. Thus, the electron concentration will raise that led to increasing the conductivity. Furthermore, thermal annealing is the useful technique to improve the crystalline and minimize the defect in the semiconductor. Also, annealing had been used to stimulate the Antimony doping and change the conductivity type from n-type to p-type in Sb-doped ZnO. Also, annealing in the presence of Argon enhance the doping of Arsenic (As) in ZnO and as a result the charge carriers change from free electrons to holes. Annealing ZnO above 227 °C in the absence of O₂ gas will activate a conductive layer on the surface.

2.3 Photoconductivity of ZnO

The photoconductivity is one of the most important phenomena that observed in ZnO. Photoconduction is a rise in the conductivity due to the absorption of the photon. Due to the absorbing of the photon, the electron in valence band will excite and transfer to the conduction band to react as a free electron as illustrated in Figure 2.5. Typically, when a ZnO crystal is subjected to light an increase of the conductivity will be reported.

The photoconductivity is affected by a number of parameters such as the density of charge carriers, the generation, lifetime, and recombination of carriers, the temperature, and the energy of the light illumination. To understand the photoconductivity, the exciton theory in semiconductors and the persist photoconductivity, including trapping and recombination, should be discussed.
Figure 2.5: Convention to explain the photoconductivity phenomenon in semiconductors when it exposed to light.

2.3.1 The Exciton Theory in Semiconductors

An exciton is the excitation state as a result of absorbing a photon while the semiconductor exposed to the light. Under this circumstance, if an electron in the valence band gains energy higher than the energy of the band gap, the electron will excite and jump from the valence band to the conduction band leaving behind a hole. The exciton, which is an electron-hole pair, will generate optically. In this case, the electron bonds with the hole due to the Coulomb force as indicated in Figure 2.6.

The exciton has a long lifetime in Zinc Oxide. Thus, it takes time before dissociation. The large exciton binding energy of about 60 meV handles extending the electron-hole pair’s duration of life.
2.3.2 Persistent Photoconductivity of ZnO

The persistent photoconductivity (PPC) is a decline in the conductivity due to turning off the light illumination. As stated in the previous section, in ZnO the exciton has a long lifetime that leads to the prevention of the recombination process to happen right after the light resource switch off as might be expected.
Chapter 3
Experimental Techniques

3.1 Sample Preparation
Sb-doped ZnO wires were prepared using the thermal evaporation technique, which is a simple process at low cost and temperature. A particular mass ratio of Zinc powder and Antimony trioxide powder were mixed in a vortex mixer for 30 min at speed 10, as shown in Figure 3.1 (c). The mixture was poured into a crucible with a lid and loaded into a furnace at 900 °C for two hours as illustrated in Figures 3.1 (a) and (b) respectively. As shown in Table 3.1, ZnO:Sb wires were obtained using two different growth conditions. The first condition (i.e. cooling the sample down to room temperature naturally) enables the growth of ZnO:Sb microwires. In the second condition, the cooling time is controlled from 900 °C to 600 °C for some samples, where the temperature is decreased by 3.3 °C per minute. Additionally, the temperature was held at 800 °C, 700 °C and 600 °C for 15 min/each and then cooled naturally to room temperature. As a result, Sb-doped ZnO wires were produced in nanostructures as shown by SEM images. However, slowing down the rate of cooling time to 0.83 °C per minute did not lead to the formation of right ZnO wires. Moreover, for few samples the cooling time was controlled from 900 °C to 600 °C to decrease by 10 °C per minute. Then the cooling time was slowed to 3.3 °C per minute from 600 °C to 400 °C after that the samples went to room temperature naturally. In a like manner of controlled cooling time, the temperature was held at 600 °C, 500 °C, and 400 °C for 15 minutes per each.
Figure 3.1: Equipment that was used to fabricate Sb-doped ZnO: (a) the alumina crucible, (b) the 47900 Furnace, and (c) the standard vortex mixer.

<table>
<thead>
<tr>
<th>Mass Ratio Zn:Sb₂O₃</th>
<th><strong>Cooling Mode</strong></th>
<th><strong>Hold Time While Cooling</strong></th>
<th>Result</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>800 °C</td>
<td>700 °C</td>
</tr>
<tr>
<td>1:3.5</td>
<td>Natural Cooling</td>
<td>-----</td>
<td>-----</td>
</tr>
<tr>
<td>1:1</td>
<td>Natural Cooling</td>
<td>-----</td>
<td>-----</td>
</tr>
<tr>
<td>1:1</td>
<td>0.83 °C per Minute</td>
<td>60 min</td>
<td>60 min</td>
</tr>
<tr>
<td>1:1</td>
<td>3.3 °C/min (900 °C-600 °C)</td>
<td>15 min</td>
<td>15 min</td>
</tr>
<tr>
<td>2:1</td>
<td>10 °C/min (900 °C-600 °C)</td>
<td>15 min</td>
<td>15 min</td>
</tr>
<tr>
<td></td>
<td>3.3 °C/min (600 °C-400 °C)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 3.1: Experimental results of the synthesis of Sb-doped ZnO micro/nanowires at different conditions.
As depicted in Table 3.1 Sb-doped ZnO wires are successfully prepared in the natural cooling mode with an equivalent mass ratio of Zn and Sb$_2$O$_3$. Also, ZnO:Sb wires obtained in the controlled cooling mode under two conditions. The morphology of these wires will be presented in the next section.

3.2 SEM Images and Energy Dispersive Spectroscopy of Sb-doped ZnO Wires

In Scanning Electron Microscopes, the primary electrons from the electron beam interact with the specimen’s atoms to generate different types of signals in different energy levels. To study the morphology and the surface topography, secondary electron signals that hit the detector produce an image. ZnO:Sb wires were inspected under different magnifications and accelerating voltages. Moreover, X-ray is another kind of signal that is used to identify the elemental components using the Energy Dispersive Spectroscopy (EDS) detector. Whenever X-rays leave the sample and hit the semiconductor crystal within the detector, they produce electron-hole pairs, so, there will be a current flow. Therefore, X-ray emission could be measured from the flowing current since they are proportional to each other. In this technique, the sample should be at a working distance of about 8.5 mm and without tilting the stage.

The topological structures and the elemental compositions will be characterized and discussed in detail for the Sb-doped ZnO micro and nanowires obtained under different conditions. First, to identify the surface morphology of ZnO:Sb wires that were prepared with natural cooling, SEM images were captured under different magnifications. According to SEM images, ZnO:Sb wires were formed in a long wire with branches. As is indicated in Figure3.2 (a), ZnO:Sb wires that have grown
under natural cooling condition established in microstructures. The diameter of the long wire is about 25 µm while it is 1.5 µm in the branches. Furthermore, EDX analysis was performed to determine the elemental compositions of Sb-doped ZnO microwires, which were obtained under the first condition. ZnO:Sb wires consist of 49 atomic % of Zn, 4 atomic % of Sb and 47 atomic % of O₂ as shown in Figure 3.2 (b).

Figure 3.2: Representation to study the morphology and the compositions of a Sb-doped ZnO wire prepared under the natural cooling mode where: (a) is SEM at 1.51 KX and 5 KV, and (b) is the EDX analysis under 30 KV.
Based on the details of the micro-wires grown using the natural cooling mode, as shown in Figure 3.2, a new approach was developed to improve the topological structures of the ZnO:Sb wires. The first group of samples synthesized under the controlled cooling mode is represented in Figure 3.3 (a). Sb-doped ZnO is produced with long primary rods of about 2 µm in diameter, and about 30 nm nanowires that grow as branches to the main rods. Furthermore, the EDX analysis showed that the long ZnO:Sb wire with 2 µm diameter consists of 22.58 atomic% of Zn, 9.7 atomic % of Sb and 67.72 atomic % of O₂ as it illustrated in Figure 3.3(b).

Figure 3.3: Studies of the morphology and the compositions of the first group of Sb-doped ZnO wires that were prepared under the controlled cooling mode where: (a) is SEM image at 42 KX and 3 KV, and (b) is the EDX analysis under 20 KV.
Due to the increase of Sb atomic %, we made a slight modification in the slow cooling mode. The 15-minute holding was made at 600 °C, 500 °C, and 400 °C instead of 800 °C, 700 °C, and 600 °C. This is called the second group of samples with the controlled cooling mode. According to SEM images, Sb-doped ZnO wires grow with diameter of 2 µm, as is illustrated in Figure 3.4(a). While Figure 3.4(b) shows that there are also some ZnO:Sb wires that grew in nanostructures with diameter and length of 600 nm and 9µm respectively. Furthermore, EDX analysis was used to determine the composition of ZnO:Sb obtained in this case. So, the composition was as follows: 30.43 atomic % of Zn, 6.91 atomic % of Sb and 62.66 atomic % of O₂ as illustrated in Figure 3.4(b).

![Figure 3.4](image)

Figure 3.4: Illustration of the morphology and the composition of the second group of Sb-doped ZnO wires that were prepared under the controlled cooling mode where: (a) is an SEM image at 21 KX and 3.99 KV, (b) is an SEM image at 27.9 KX and 3.99 KV, and (c) is the EDX analysis under 20 KV.
Overall, based on the images shown above the following assumptions can be made. The slow cooling mode was demonstrated to improve the microwires into the nanoscale. Additionally, to avoid the increase of Sb atomic % the hold time should be made at different temperatures. The hold time was at 800 °C, 700 °C, and 600 °C. Thus, the Sb % increased because Sb$_2$O$_3$ has a melting point of 656 °C and keeping the temperature close to its melting point extended the interaction time. Holding the temperature below the Sb melting point made it possible to synthesize Sb-doped ZnO wires in nanoscale without increasing Sb atomic % in the fabricated wires.

### 3.3 Annealing Effect and Photoconductivity Measurements

Measurements were carried out to investigate the annealing effect on the electrical properties of Sb-doped ZnO wires. For this analysis, three kinds of Sb-doped ZnO devices were designed. To prepare the first device using UV photolithography, features with a variety of separations of about 20 μm, 100 μm, 300 μm, and 700 μm were defined on a SiO$_2$ substrate. After that, on top of these patterns 30 nm of Cr were thermally deposited in a vacuum chamber. A single ZnO:Sb wire was then connected between two of the square features with a separation of 700 μm using H20E EPO-TEK Silver Conductive Epoxy. Two Au wires were used to connect to the square features in order to measure the voltage across Sb-doped ZnO wire. After that, the substrate was heated to 150 °C for 5 minutes in order to cure the epoxy and allow it to become conductive. SEM image of the first kind of Sb-doped ZnO devices is illustrated in Figure 3.5 (b).

The second kind of Sb-doped ZnO devices was prepared by fixing two rectangular sheets of Cu on SiO$_2$ a substrate using H20E Silver Conductive Epoxy. A gold wire connected to each sheet was used to measure the voltage across the ZnO:Sb wire. Then the substrate was heated to 150 °C for 5 minutes, including the copper sheets
and the gold wires, to allow the epoxy to cure and get harder and conductive. After that, a small area of Indium (In) is applied to the top of each Cu sheet using the soldering station. Finally, a single Sb-doped ZnO wire was connected between the Cu sheets and a small drop of the Ag epoxy added on both ends of the wire. The epoxy gets harder in the first 20 to 30 minutes of annealing after the measurement started. The SEM image of the second kind of Sb-doped ZnO devices is shown in Figure 3.5(c).

The third type of Sb-doped ZnO devices was prepared by inserting an alumina (with 3mm in thickness and 1×0.6 inch) in between two of U-shaped Al (1×1 inch, 0.5 inches in thickness). One gold wire was attached to each of the Al pieces using the Ag epoxy and heated to enable the epoxy to cure. Then, a small area of In was applied on top of each Al using the soldering station. After that, a selected ZnO:Sb wire was loaded between the In sheets. The Sb-doped ZnO wire was fixed by adding a small drop of Ag epoxy. An optical image of the third kind of ZnO:Sb devices is shown in Figure 3.5(d). The measurement electric circuit for any of the three kinds of devices is illustrated in Figure 3.5(a). One of the gold wires is connected to the positive side of a battery of about 1.376 V and at the same time connected in parallel with the positive terminal of the voltmeter. Likewise, the other gold wire connected in serial through an external resistor of about 1.5 MΩ with the negative terminal of the battery, and connected in parallel with the negative terminal of the voltmeter. Additionally, Labview software was used to measure the voltage of the sample as a function of annealing time. The measurements were carried at different annealing temperatures in air.
Figure 3.5: (a) Schematic cartoon of the electric circuit that was used to study the annealing effect in Sb-doped ZnO wires under different conditions. (b) Scanning Electron Microscope image of the first kind of ZnO:Sb devices at 70 X magnification, 7 mm working distance, and 5 KV accelerating voltage. (c) Scanning Electron Microscope image of the second kind of Sb-doped ZnO devices at 135 X magnification, 8.3 mm working distance, and 5 KV accelerating voltage. (d) An optical picture of the third type of Sb-doped ZnO devices including the two contacts of gold wires.

While studying the annealing effect on Sb-doped ZnO wires, the conductivity changed depending on the surrounding light in the lab and the effect of light was observed. A number of techniques were used to insulate the annealing effect from
the light effect in Sb-doped ZnO wires. Figure 3.6(a) represents the first method, in which a cap of foil was used to cover the sample from the light to study the dark conductivity while annealing. In the second technique, a rectangular box of Al (6×2×1.5 inch) was built to block the light as indicated in Figure 3.6 (b). The third technique was using the 47900 Furnace to block the light. Using the furnace also helped to eliminate the temperature fluctuations. Figure 3.6 (c) shows the setup of the electric circuit inside the oven.

Figure 3.6: (a) A picture of the foil cap that was initially used to block the light. (b) A picture of the Al box, which was used as a second technique to reduce the effect of light. (c) Picture of the electric circuit inside the furnace that was also used to separate the light effect from the annealing effect.
3.4 Thermoelectric Effect Measurement

A simple setup was built, which is illustrated in Figure 3.7(b), to investigate the type of conductivity. A single ZnO:Sb wire was connected between the hot terminal and cold terminal. The hot terminal was connected through an external resistor with the positive probe of a digital voltmeter. Also, the cold terminal is connected to the negative terminal of the voltmeter as shown in Figure 3.7(a).

Figure 3.7: (a) Schematic diagram of the used electric circuit in the thermoelectric effect measurement. (b) A photo of the setup that was used in the hot point probe experiment.
Chapter 4  
Results and Discussions

4.1 Influence of In-situ Annealing on The Electrical Properties of ZnO:Sb Wires at Different Temperatures

The effect of in-situ annealing on Sb-doped ZnO wires was investigated in this thesis under different temperatures in air. Figure 4.1 represents the annealing influence on ZnO:Sb wire at two different values of temperature, which are 150 °C and 200 °C, and the annealing durations are 132 minutes and 348 minutes respectively. Before the stability of the temperature occurred, the resistivity of Sb-doped ZnO wire declined sharply as a function of temperature following the equation:

\[ \rho = \rho_0 e^{-\frac{E_g}{2KT}}. \]

Even after the temperature became stable, the resistivity of ZnO:Sb continued to decrease gradually as a function of annealing time. The decline of the resistivity is likely due to the thermally activated desorption of oxygen atoms from the surface of the wire.. Another potential reason for the drop in the resistivity is the reduction of defects in ZnO:Sb wires due to annealing.
Figure 4.1: A graph of the resistivity of Sb-doped ZnO wires as a function of annealing time during the wire anneal at 150 °C for 132 minutes in ambient room light and then at 200 °C for 348 minutes in the light.

4.1.1 The Effect of In-Situ Annealing on the Electrical Properties of ZnO:Sb Wires at 150 °C

Figure 4.2 shows how in-situ annealing of ZnO:Sb wires affects the resistivity at 150 °C in the air. For this analysis, two groups of ZnO:Sb wires used as follows: annealed ZnO:Sb wire in dark (the red line) and annealed ZnO:Sb wire in light (the blue line). The behavior of both ZnO:Sb groups was recorded during annealing for 20 hours to determine an ideal condition to possibly change the type of charge carriers from n-type to p-type.
Figure 4.2: The resistivity as a function of annealing time curves of ZnO:Sb wires at 150 °C. The red line is for in-situ annealing in the dark and the blue line is for in-situ annealing in the light (ambient room light).

For the annealed ZnO:Sb wire in the light, the resistivity reduced sharply to half of its value in the first hour resulting from the rapid increase in the temperature. Later a gradual decrease in the resistivity of ZnO:Sb wire was recorded. However, annealing ZnO:Sb wire in the dark shows a rapid decline of the resistivity in the first hour. After that, the resistivity started to increase for nine hours, and for the last ten hours the resistivity dropped progressively. To study the ambiguous behavior of annealing ZnO:Sb and investigate the reason for increasing the resistivity upon annealing in the dark, some influencing factors on the resistivity of ZnO:Sb should be discussed. The resistivity of ZnO:Sb varies depending on the following factors:
I. Increasing the temperature according to equation (4.1) leads to a sharp decline in the resistivity of ZnO:Sb as illustrated in region (i) of Figure 4.3 and in Figure 4.4 (a).

II. Switching the surrounding environment from light to dark led to the persistent photoconductance (PPC) phenomenon, in which the photoconductivity decays slowly when turning the light off and that increases the resistivity as shown in region (ii) in Figure 4.3 and Figure 4.4(b).

III. Annealing influence on ZnO:Sb wires which led to a moderate drop in the resistivity as represented in region (iii) of Figure 4.3 and Figure 4.4(c).

Figure 4.3: Schematic diagram to explain the possible factors that might affect the resistivity of Sb-doped ZnO wires.
Figure 4.4: (a) The resistivity and temperature curves as functions of time to explain factor (I), (b) the resistivity as a function of annealing time curve at 150 °C after switching light off to reveal factor (II), and (c) Diagram of ZnO:Sb behavior upon annealing at 150 °C to represent factor (III).
According to Figure 4.4(b) the resistivity of ZnO:Sb wires could increase as a result of the persistence photoconductivity when the light is turned off. In the dark annealing case, the wires were fixed in the light and then connected to the electric circuit inside the oven (in the dark) to study the in-situ annealing effect. Therefore, the increasing of the resistivity after the first hour of annealing might be resulting from the decay of the photoconductivity. An important other possible reason for the rise in the resistivity of ZnO:Sb wires might be a gradual change in the majority charge carriers from n-type to p-type. Changing the charge carriers type might be resulting from the interaction with Oxygen molecules, so when an electron is trapped on the surface, it ionizes O$_2$ leaving an unpaired hole. As the number of trapped electrons increases the resistivity increases, and the unpaired holes increase too. At the moment the number of holes becomes larger than the number of free electrons, the conductivity type switches from n-type to p-type. After that, the resistivity of the ZnO:Sb wire starts to decrease gradually as the density of holes increases.

In order to determine whether the PPC is the reason of the increase in the resistivity of Sb-doped ZnO wires or not, ZnO:Sb Wires were kept in the dark before the annealing started. Three groups of ZnO:Sb wires were used as follows: (I) Annealing ZnO:Sb wires after staying in the dark for two hours, which is represented by the red line in Figure 4.5, (II) Annealing ZnO:Sb wires after staying in the dark for five hours (the blue line in Figure 4.5), and Annealing ZnO:Sb wires after waiting in the dark for 22 hours( the green line in Figure 4.5). All ZnO:Sb groups show the same behavior, as indicated in Figure 4.5, which proves that the PPC is not likely to be responsible for the peak in the resistivity upon annealing in dark at 150 ºC.
Figure 4.5: The resistivity as a function of annealing time for three different groups as following: The red line is for a ZnO:Sb wire after staying two hours in the dark at room temperature before starting the in-situ annealing at 150 °C. The blue line is for a ZnO:Sb wire after waiting five hours in the dark at room temperature before starting the in-situ annealing at 150 °C. The red line is for a ZnO:Sb wire after remaining 22 hours in the dark at room temperature before beginning the in-situ annealing at 150 °C.

4.1.2 The Effect of In-Situ Annealing on The Electrical Properties of ZnO:Sb Wires at 200 °C

To confirm that the PPC is not the causative of increasing the resistivity, the in-situ annealing was also done at 200 °C in both light and dark during five hours. For annealed ZnO:Sb wires in the light, the resistivity decline rapidly in the first ten minutes, after that a moderate drop was recorded as illustrated in Figure 4.6 (the red line). However, for the annealed ZnO:Sb wires in the dark a gradual decrease
in the resistivity was recorded. No increase, or peak, in the resistivity of ZnO:Sb was observed in five hours of annealing in the dark. This further suggests that the PPC is not the reason for the peak in the resistivity at 150 °C in the dark.

![Graph showing resistivity over time for ZnO:Sb wires at 200 °C in light and dark.]

Figure 4.6: The resistivity as a function of time of ZnO:Sb wires at 200 °C in the light (red line) and in the dark (blue line).

4.2 ZnO:Sb Photoconductivity and Persistent-Photoconductivity

The resistance of Sb-doped ZnO wires varies depending on the surrounding illuminations as mentioned in section 3.3 in the previous chapter. Figure 4.7 shows the photoconductivity and the persistent photoconductivity of individual ZnO:Sb wire that was annealed for 23 hours in dark at 200 °C before the light effect was examined. At the moment the light was turned on the resistance of ZnO:Sb wire decreased sharply and then a gradual decline in the resistance was observed. In
similarity, when the light was turned off the photoconductivity of ZnO:Sb decayed rapidly and then a moderate decline in the photoconductivity was observed. Light effect on Sb-doped ZnO wires were investigated while annealing and at room temperature. The data of both cases will be discussed in details in the two following sections.

Figure 4.7: Resistance as a function of annealing time showing that the ZnO:Sb wire is influenced by the lab illuminations while annealing at 200 °C.

4.2.1 ZnO:Sb Photoconductivity and Persistent-Photoconductivity While Annealing at 150 °C

Figure 4.8 indicates the effect of visible illuminations in Sb-doped ZnO while annealing in the air at 150 °C for four groups of individual wires during 90 minutes. The Four groups of ZnO:Sb wires were as the following: an as grow ZnO:Sb wire, an annealed ZnO:Sb wire at 150 °C for 15 hours in the dark, an annealed ZnO:Sb wire at 150 °C for 20 hours in the dark, and an annealed ZnO:Sb wire at 150 °C for 25 hours in the dark. The as grow Sb-doped ZnO wire showed
the highest response rate to visible light and the largest decrease in the resistivity during the exposure time compared to the other annealed ZnO:Sb wires. The resistivity of the as grown ZnO:Sb wire declined to about half of its value while exposed to the visible light for 90 minutes. Conversely, annealing Sb-doped ZnO wire up to 25 hours at 150 °C minimized the light effect and showed the lowest response rate to the light.

Understanding the mechanism of the reaction between ZnO:Sb wires and Oxygen molecules is necessary to explain the photoconductivity behavior of ZnO:Sb wires. Before the electric field is applied on Sb-doped ZnO wires, the free electrons ionized the Oxygen molecules near the ZnO:Sb surface. Thus, ZnO:Sb wires became highly resistive, which lead to the decrease of the charge carriers, at room temperature. The interaction between the free electrons and the Oxygen molecules, in the absence of electric field, indicated by the following equation:

\[ \text{O}_2^{\text{(gas)}} + e^- \rightarrow \text{O}_2^{\cdot} \text{(adsorb in the surface).} \]

For all Sb-doped ZnO wire groups, a huge reduction happened in the first six minutes of switching the illumination on. The fast decrease in ZnO:Sb, right after the light is turned on, is resulting from the production of electron-hole pairs when valence band’s (or more likely impurity bands’) electrons absorbed photons and transitioned to the conduction band, so the number of charge carriers increases.\(^{19}\) Therefore, the holes are trapped on the surface to neutralize the Oxygen ions leaving behind unpaired electrons in the conduction band, the interaction is given by the following equation:

\[ \text{O}_2^{\cdot} \text{(adsorb in surface)} + h^+ \text{(hole)} \rightarrow e^- + \text{O}_2 \text{(emitting g.)}. \]

At the same time, unpaired electrons are governed by the electric field to move towards the positive terminal as charge carriers, which increases the conductivity sharply at the moment the light was turned on. In fact, that explains the faster
decay for the as grown Sb-doped ZnO wire, which has a huge number of Oxygen ions in the surface, as compared to the annealed ZnO:Sb wires since there are more holes trapped to the surface in order to discharge the Oxygen ions. The trapping of holes made it possible to increase the density of charge carriers, caused by producing unpaired electrons.

Figure 4.8: The resistivity of Sb-doped ZnO wires as a function of time in order to study the photoconductivity effect with a variety of annealing durations when the samples are subjected to the visible illumination (using a light bulb) at 150 °C using four groups of ZnO:Sb wires as the following: (blue line) the as grow ZnO:Sb wire, (red line) the annealed ZnO:Sb wire for 15 hours in the dark at 150 °C, (green line) the annealed ZnO:Sb wire for 20 hours in the dark at 150 °C, and (purple line) the annealed ZnO:Sb wire for 25 hours in the dark at 150 °C.
From Figure 4.9 it can be seen that the decay rate of the photoconductivity of the annealed wire, when the surrounding light is turned off, is much slower than the as grow wire. In fact, the as grown ZnO:Sb wire takes 12 minutes to go back to the same resistivity before the illumination turns on for 90 minutes. However, annealed ZnO:Sb wires for 15 hours, 20 hours, and 25 hours take 78 minutes, 204 minutes, and 264 minutes, respectively, to return to the same resistivity before the light was turned on. Increasing the annealing duration increases the persistence photoconductivity rate. Moreover, all ZnO:Sb wires showed that the largest change of the resistivity and the fastest photoconductivity decay rate happened at the first minute after switching the light off immediately. The decay of the photoconductivity results from the recombination process in which the electron recombines with the hole. The recombination process reduces the charge carriers density, which explains the increase of the resistivity after turning the light off.
Figure 4.9: The resistivity of Sb-doped ZnO wires as a function of duration in order to study the persistent-Photoconductivity behavior with a variety of annealing times after wires are exposed to light for 90 minutes at 150 °C using four groups of ZnO:Sb wires as the following: (blue line) the as grown ZnO:Sb wire, (red line) the annealed ZnO:Sb wire for 15 hours in the dark at 150 °C, (green line) the annealed ZnO:Sb wire for 20 hours in the dark at 150 °C, and (purple line) the annealed ZnO:Sb wire for 25 hours in the dark at 150 °C.

4.2.2 ZnO:Sb Photoconductivity and Persistent Photoconductivity at Room Temperature

Figure 4.10 Shows the behavior of ZnO:Sb wires at room temperature when exposed to the light from a compact fluorescent light bulb for Three hours to record the light effect on the resistivity. It also shows the persistent photoconductivity decay after turning the visible light illumination off. Two groups of ZnO:Sb wires were used in this study as the following: annealed ZnO:Sb wire at 150 °C in the dark for 21 hours and then cooled down to room temperature before the light is turned on (the blue line), and annealed ZnO:Sb wire at 150 °C in the
dark for 43 hours and then cooled down to room temperature before the light is switched on (the red line). As indicated in Figure 4.10, in the first 20 minutes of light exposure the resistivity of ZnO:Sb wires dropped to the half of its value at the moment right before turning the light on. Then, a progressive reduction in the resistivity of Sb-doped ZnO wires was recorded. In contrary, at the time that the illumination was turned off, the resistivity of ZnO:Sb wires started to rise gradually. The photoconductivity decay took about 17 hours before going back to the same value of resistivity before the light was turned on. The annealing and cooling process helped to increase the Sb-doped ZnO sensitivity to light, and at the same time contributed to slow the decay of photoconductivity after the light source switch off.

Figure 4.10: A representative diagram of the photoconductivity as a function of light exposure duration of ZnO:Sb wires under the visible illumination at room temperature and the decay rate of the photoconductivity as a function of time after the light was turned off at room temperature as well for two groups of ZnO:Sb wires as the following: the annealed ZnO:Sb wire at 150 °C for 21 hours in the dark and then cooled down to room temperature (the blue line). The annealed ZnO:Sb wire at 150 °C for 43 hours in the dark and then cooled down to room temperature (the red line).
4.3 Hot Point Probe Measurement of ZnO:Sb Wires to Determine The Conductivity Type

The thermoelectric effect was used to determine the type of charge carriers. In this technique a GaMnAs thin film sample, which is a p-type semiconductor, was used as a standard or reference to compare its behavior with the behavior of ZnO:Sb samples for more confirmation. In the experiment, the data was collected for 300 Sec. In the first ten seconds the data was measured at room temperature for both positive and negative probes. For 170 seconds, a hot copper block was placed in contact with the positive terminal. By replacing the hot copper block with a cold copper block, the positive probe cooled down to room temperature for the last 120 seconds. As indicated in Figure 4.11 (a), when the hot source is placed on the positive terminal of GaMnAs, a positive voltage was measured across the sample. As a result of the potential difference, a positive current flows through the sample (Figure 4.11 (b)). On the other hand, placing the hot copper block on the positive terminal of Sb: ZnO wires caused a negative voltage across the wires as is shown in Figure 4.11 (e). Therefor, a negative current flows as illustrated in Figure 4.11(f). The measurement was repeated at different temperatures of the hot resource, which were 50 °C, 75 °C and 100 °C.

For more persuasive results, the hot copper block was placed on the negative terminal and then the experiment was repeated using the same steps. In GaMnAs, a negative voltage was measured as represented in Figure 4.11 (c). Additionally, as illustrated in Figure 4.11 (d), a negative current was flowing through the GaMnAs sample. However, as indicated in Figure 4.11(g), when the hot copper block was placed on the negative probe of ZnO:Sb wires a positive voltage was measured and also, a positive current flowed across the sample as shown in Figure 4.11(h). Therefore, it is obvious that Sb-doped ZnO is an n-type semiconductor.
In fact, when the hot source was placed on the positive terminal, the majority charge carriers, which are the free electrons in ZnO:Sb wires, move from the hot terminal to the cold terminal, while the holes move from the cold to the hot end. So, the current moves from the cold terminal, which is negative, to the hot terminal, which is positive. Thus, a negative current was flowing to prove that Sb-doped ZnO is an n-type semiconductor. Moreover, ZnO:Sb wires showed the opposite behavior of GaMnAs thin film, which is p-type. This proves that the charge carriers in ZnO:Sb wires are free electrons.
Figure 4.11: The left column represents the behavior of GaMnAs sample as the following: (a) the generated voltage as the positive terminal was heated, (b) the flowing current as the positive terminal was heated, (c) the generated voltage as the negative terminal was heated and, (d) the flowing current as the negative terminal was heated. While the right column illustrates the behavior of ZnO:Sb sample as following: (e) the generated voltage as the positive terminal was heated, (f) the flowing current as the positive terminal was heated, (g) the generated voltage as the negative terminal was heated and (h) the flowing current as the negative terminal was heated.\textsuperscript{33}
Chapter 5
Conclusions

In this study, the electrical properties of Sb-doped ZnO Nano/microwires were investigated. ZnO:Sb wires were fabricated by the thermal evaporation method at 900 °C in an alumina crucible. The surface morphology was studied using Scanning Electron Microscopy (SEM). The elemental components were determined using X-ray Energy Dispersive Spectroscopy (EDX). Sb-doped ZnO wires were successfully grown using thermal evaporation in diameters between 25 µm and 30 nm with atomic % of Antimony between 9 % and 4 %. The conductivity type of Sb-doped ZnO was also studied using thermoelectric effect measurements. The kind of charge carriers in Sb-doped ZnO wires was found using the hot point probe to be free electrons. Moreover, the in-situ annealing effect in ZnO:Sb wires was used to activate the Sb dopant. Also, the electrical properties of ZnO:Sb were studied by observing the behavior of the wires under low-temperature annealing in the air. Annealing ZnO:Sb wires in the dark at 150 °C was found to be the most promising strategy to change the conductivity type from n-type to p-type. Furthermore, the photoconductivity and the persistent photoconductivity were investigated using the visible light while annealing and at room temperature after annealing as well. Low-temperature Annealing followed by cooling to room temperature was found to be an effective technique to improve the photoconductivity and the PPC.
Chapter 6
Future Work

In this work, the annealing effect on the behavior of Sb-doped ZnO wires was only studied in air under the atmospheric pressure. Due to the sensitivity of ZnO:Sb to the surrounding gas, especially Oxygen gas, it would be interesting for continued study to investigate the annealing effect on the behavior of ZnO:Sb wires in different environments and vacuum mainly. That will separate the effect of annealing from the gas sensing response.

Further research using ZnO:Sb NW-Field Effect Transistor (FET) will be required to prove the hypothesis that suggests the charge of carrier type in Sb-doped ZnO wires from n- to p- under annealing at 150 °C in the dark. The FET is a promising technique to confirm the conductivity type.

Also, ZnO:Sb wires in nanoscale are necessary to extend the knowledge of light sensitivity and even the gas sensitivity. More manipulation in the technique of synthesis of Sb-doped ZnO wires will be needed to obtain ZnO:Sb Nano-Wires.
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