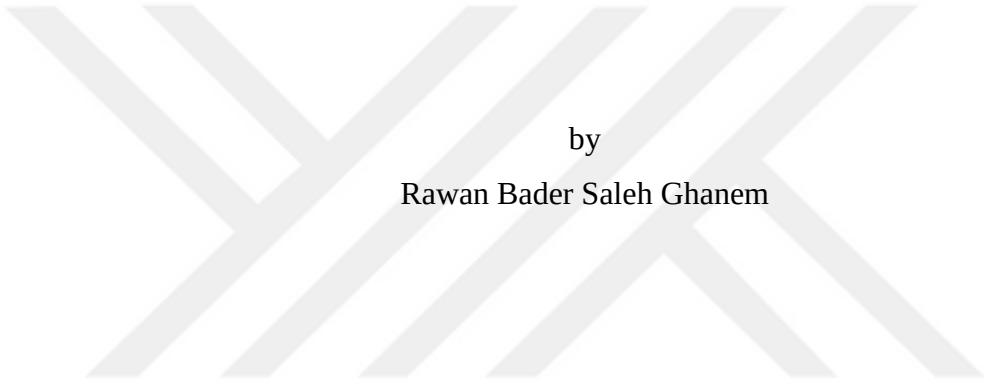


PREPARATION AND CHARACTERIZATION OF ZNO NANOWIRES ON ITO-
GLASS AND ITO-PET SUBSTRATES



by

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PREPARATION AND CHARACTERIZATION OF ZNO NANOWIRES ON ITO-
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ABSTRACT

PREPARATION AND CHARACTERIZATION OF ZNO NANOWIRES ON ITO-GLASS AND ITO-PET SUBSTRATES

The study of nanotechnology involves both understanding the materials as well as controlling the processing conditions of these materials at the nanoscale. In the class of nanostructures, semiconducting nanowires are of high interest because of their extraordinary properties and promising applications. The uniqueness mainly arises from the surface-to-volume ratio being higher than that of most nanostructures. Of all semiconducting materials, zinc oxide exhibits a large excitation binding energy and wide bandgap, making it highly desirable to be used for transistors, photodetectors, and multipurpose piezoelectric nanogenerators. Vertically aligned zinc oxide nanowires can be synthesized using a variety of techniques, the hydrothermal growth method being one of the easiest and most affordable and low operating synthesis techniques.

In this thesis, vertically aligned zinc oxide nanowires are synthesized onto indium tin oxide coated PET and glass substrates via the hydrothermal growth technique. The growth conditions were optimized with parameters such as growth temperature, annealing temperature, and solution concentration not changing. Other experimental parameters such as seeding layers and growth durations varied throughout. The morphology and microstructures of the zinc oxide nanowires synthesized are investigated with the use of X-ray diffraction and scanning electron microscopy. Furthermore, the transmission percentages are examined with the use of ultraviolet and visible light spectrometer as well as the surface roughness is measured with the use of atomic force microscopy. Electrical conductivity measurements were taken to assess the quality of the substrates and their possible use in applications. Between the growth conditions and parameters and the growth of the zinc oxide nanowires, this thesis presented a strong correlation in terms of the different results achieved.

ÖZET

ITO-CAM VE ITO-PET ALTIKLAR ÜZERINE KAPLANAN ZNO NANOTELLERİN HAZIRLANMASI VE KARAKTERİZASYONLARI

Nanoteknoloji çalışmaları; malzemelerin özelliklerinin ve proses parametrelerinin nanoboyutlarda anlaşılması ve control edilmesidir. Nanoyapılar sınıfında, yarı-iletken nanoteller özellikleri ve ilgi çekici uygulama potansiyelleri açısından en çok ilgi ve dikkat çeken malzemelerdir. Bu nanotellerin spesifik özellikleri,, yüzey/hacim oranının diğer nanoyapılı malzemelere göre çok yüksek olmasındandır. Tüm yarı-iletken malzemeler içinde ZnO yüksek uyarılma enerjisi ve geniş band aralığından dolayı, özellikle transistörlerde, fotodetektörlerde ve çok amaçlı piezo-jeneratörlerde kullanımları ilgi çekmektedir. Dik olarak yönlendirilmiş ZnO nanoteller, farklı tekniklerle üretilebilmektedir ancak hidrotermal büyüme metodu, düşük sıcaklıklarda, ucuz ve en kolay üretim yöntemi olarak ortaya çıkmaktadır.

Bu tez çalışmasında; dik olarak yönlendirilmiş ZnO nanoteller, ITO kaplanmış Cam ve PET altlıklar üzerine hidrotermal büyüme tekniği kullanılarak büyütülmüşlerdir. Nanotel büyütmede; büyütme sıcaklığı, tavlama sıcaklığı ve çözelti konsantrasyonu sabit tutulurken, çekirdek tabaka sayısı ve büyütme süreleri değişken parametreler olarak tutulmuşlardır. Sentezlenen ZnO nanotellerin morfoloji ve mikroyapıları, XRD ve SEM teknikleri kullanılarak incelenmiştir. Ayrıca, altlıkların ışık geçirgenlikleri UV-VIS spektrometresi ve yüzey pürüzlülükleri AFM kullanılarak ölçülmüştür. Elektrik iletkenliği ölçümleri, altlıkların iletkenliklerini ölçmek ve potansiyel uygulama alanlarını belirlemek için uygulanmıştır.

Bu tez çalışmasında; hidrotermal yöntem kullanılarak nanotel büyüme şartlarının ve parametrelerinin, ZnO nanotel büyütmedeki etkileri incelenmiş ve aralarında çok güçlü ilişkiler olduğu gösterilmiştir.

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LIST OF SYMBOLS/ABBREVIATIONS

1D	One-dimensional
2D	Two-dimensional
3D	Three-dimensional
1L	One layer
3L	Three layers
5L	Five layers
10L	Ten layers
AAO	Anodic aluminum oxide
AFM	Atomic force microscopy
Ag/AgCl	Silver/Silver chloride
Ar	Argon
°C	Degrees celsius
(CH ₂) ₆ N ₄	Methenamine
cm ⁻¹	Reciprocal centimeter
CO	Carbon monoxide
DC	Direct current
DI	Distilled
e ⁻	Electron
EDS	Energy dispersive X-Ray spectroscopy
eV	Electron-volt
FESEM	Field emission scanning electron microscopy
g/mol	Gram per moles
gcm ⁻³	Grams per cubic centimeter
CH ₃ OH	Methanol
HCl	Hydrochloric acid
HMTA	Hexamethylenetetramine
H ₂ O	Water
Hz	Hertz
ICDD:	International centre for diffraction data
Ind ₂ O ₃ : Sn	Indium (III) oxide: tin
IR	Infrared

ITO	Indium tin oxide
kV	Kilovolt
M	Molar
MEMS	Micro electro-mechanical systems
meV	Mega electron-volt
min	Minutes
mL	Milliliter
mM	Milli-molar
mV	Millivolt
NaOH	Sodium hydroxide
NH ₃	Ammonia
NH ₄ ⁺	Ammonium ions
nm	Nanometer
NO	Nitric oxide
NO ₃ ⁻	Nitrate
O ₂	Dioxygen
OH ⁻	Hydroxide
PC	Polycarbonate
PET	Polyethylene terephthalate
ppm	Parts per million
Pt	Platinum
Ra	Arithmetical mean roughness
rpm	Revolutions per minute
S	Siemens
SEM	Scanning electron microscopy
SnO ₂	Tin (IV) oxide
TCO	Transparent conducting oxides
UCNP	Upconversion nanoparticles
UV	Ultraviolet
UV-VIS	Ultraviolet-visible spectroscopy
VLS	Vapor-liquid-solid
W	Watts
XRD	X-Ray diffraction

ZAD	Zinc acetate dihydrate
Zn	Zinc element
Zn^{2+}	Zinc ion
$\text{Zn}(\text{NO}_3)_2$	Zinc nitrate
$\text{Zn}(\text{O}_2\text{CCH}_3)(\text{H}_2\text{O})_2$	Zinc acetate dihydrate
$\text{Zn}(\text{OH})_2$	Zinc hydroxide
ZnO	Zinc oxide
μm	Micrometer
α	Gamma
Ω	Ohm
Ωm	Ohm-meter
$^\circ$	Degree
θ	Theta

1. INTRODUCTION

In the world of science and technology, there have been many developments and progression in device manufacturing and performance, precisely in the field of electronics. These advancements depend majorly on studying the nanoscale more closely and understanding the behaviors of materials under certain conditions. For these reasons, the number of applications has drastically increased as materials tend to behave differently at smaller scales, and researchers can design, synthesize, analyze and develop different kinds of nano-materials. Depending on what the desired outcome is, its properties and functionality of it is determined by its size, showing the importance of nanotechnology studies. In the case of electronics, semiconducting materials are used as the essential constituents and nanotechnology can be applied here when devices are fabricated at smaller scales. To be able to synthesize nanostructures, researchers have studied multiple methods to acquire specific properties.

Nanostructures are classified into four main groups: one-dimensional, two-dimensional, three-dimensional, and zero-dimensional structures, each exhibiting specific properties and behaviors, which are further explained below. Nanowires are one of the most synthesized one-dimensional structures for the reasons of their distinctive behaviors and properties. Another feature that makes nanowires desirable to investigate is their ability to have either semiconducting or metallic natures, with zinc oxide nanowires being the most fabricated. When working with optoelectronic applications, zinc oxide nanowires can be used as the material choice because of the bandgap being wide (3.37eV) and excitation binding energy (60 meV) being high at room temperature [1]. There are many methods to synthesize zinc oxide nanowires that have been developed, some of which are high in costs such as vapor deposition and pulsed laser deposition, and require high processing temperatures while others are simpler processes with lower processing temperatures. The growth of ZnO nanowires can be either assisted onto a substrate or unassisted, but the presence of a substrate has proven to produce good quality vertically aligned nanowires. The hydrothermal growth process is an example of a simpler synthesis technique and is known for its low processing temperatures while producing high-quality nanowires. Many benefits come with using the hydrothermal method to synthesize zinc oxide nanowires such as controlling the

morphologies of the produced nanowires by manipulating the growth conditions. As well as it permits growth on larger substrates more than most growth techniques. Since the growth is conducted in aqueous solutions, it is an environment-friendly synthesis technique, meaning a vacuum is not needed and no toxic gases are released into the environment. Recent studies have shown the development of ZnO applications into piezoelectric nanogenerators for harvesting energy from the medium [2]. Because of the semiconducting and piezoelectric properties of zinc oxide nanowires, the mechanical deformation that takes place can be converted into electric potential. The quantity of energy that can be converted is typically low, microwatts to a few milliwatts, however, it is sufficient to be used in MEMS (micro-electro-mechanical system) sensors or wearable electronics and intrinsic medical devices. Depending on the application, different substrates can be used for the growth to take place. Typically, thermal conductive oxide coated substrates are used, glass and polyethylene terephthalate (PET) to ensure that there is enough electrical conductivity going through the substrates. Due to the flexibility of the PET material, it allows for a wider range of applications [3].

In this study, the hydrothermal method was implemented to grow zinc oxide nanowires on indium tin oxide coated substrates, both glass, and PET. This technique is very useful because it allows the researchers to manipulate the growth conditions in the experiment to produce nanowires with different properties. Using both glass and PET substrates to grow zinc oxide nanowires were done to test the difference in the performance and quality of the nanowires produced. The hydrothermal growth method, a solution-phase synthesis, can be described as a two-step growth mechanism, a seeding step, and a growth step. The seeding step consists of a coating of a thin layer onto the substrate to stimulate the growth with a seeding solution usually composed of zinc acetate and isopropanol. After undergoing an annealing heat treatment, these substrates are inserted into the growth solution consisting of an alkaline reagent and zinc acetate, set at a specific temperature, around 90°C. This allows for the production of zinc oxide nanowires which are then able to be integrated into piezoelectric nanogenerator for textile integration. The physiological movements conducted by humans are where the energy will be harvested from. The outcome of this study is of such importance because it allows for the integration of useful nanostructures into wearable electronics with minimal costs and environmental harm [4]. Piezoelectric generators are manufactured at extremely small sizes that allow for them to be implemented in many

regions, including the human body. This is important because it means that no external energy source is needed for the electronic devices to work. The first flexible nanostructured energy harvester system was developed by Gao. Et al (2007) by enlarging ZnO nanowires with the use of the hydrothermal method (1). The produced voltage was around 45 mV measured with an AFM tip. According to the literature survey conducted, it is believed that with the increase of seed layers and duration of growth time, the quality and quantity of the zinc oxide nanowires produced will improve. To test this hypothesis, a variety of seeding layers have been tested (one, three, five, and 10) on both glass and PET substrates to evaluate which would be most appropriate. The concentration of seeding solution, speed of the spin coater, the concentration of the growth solution, and growth temperature were set to be the same in all trials. As well as this, several times were tested to explore the effect of growth time on the number of nanowires produced.

In this thesis, a series of information is provided. In chapter 2, detailed information is given about zinc oxide nanowires and the different methods of synthesizing them. First, a general introduction is presented about zinc oxide, characteristics of nanowires, and zinc oxide nanowires specifically. Following this, the different kinds of zinc oxide nanowire synthesis methods are showcased in detail. Then the different types of substrates that are used to typically grow nanowires are introduced. Finally, some of the applications of ZnO nanowires are conveyed. In chapter 3 the experimental procedure for hydrothermally growing zinc oxide nanowires is presented, along with the different characterization methods that are used. Then in chapter 4, the results are discussed based on the findings from the experiment that include structural, morphological, and optoelectronic properties. Finally, chapter 5 concludes the thesis by presenting some future works relating to ZnO nanowires.

2. SYNTHESIS OF ZINC OXIDE NANOWIRES VIA HYDROTHERMAL SYNTHESIS

2.1 ZINC OXIDE

Zinc Oxide (ZnO), with a molecular weight of 81.38g/mol, originally comes from three main zinc ores which are sulfides, silicates, and carbonates. The processing of zinc oxide can be done either by using these zinc ores and concentrates or by using zinc metal. Researchers have shown that the zinc oxide compound presents high thermal conductivity at temperatures of 20°C. The electrical properties of zinc oxide describe it as an n-type semiconductor, with a wide bandgap of 3.37 eV, where the excitation of the electrons takes place from ionized zinc interstitials. The electrical conductivity of ZnO can be controlled by conducting different heat treatments or the addition of different types of cations, such as monovalent (like lithium) or trivalent (like aluminum) cations [5]. For instance, when quenching at high temperatures or increasing the concentration of the zinc interstitials, the resistivity will decrease. And in the case of heating, the zinc oxide loses oxygen leading the zinc ions to fit in the interstitial sites along with entrapped electrons. This leads to the enhancement of electrical conductivity. The crystal structure of ZnO can be either rocksalt, zinc blende, or hexagonal wurtzite structure depending on the conditions of the environment. These structures are shown in Figure 2.1 below [6]. In the case of ambient conditions and parameters, the structure that is present is the wurtzite structure mainly because of the thermal stability. The lattice constants of this structure are known as $a = b = 0.3249$ and $c = 0.52042$ nm with a specific mass density of 5.675 g cm⁻³. In the case of zinc blende, zinc oxide can be grown with cubic structures with the use of substrates. Upon crystallization, where the oxygen ions follow the alignment of a hexagonal closed packed structure, with the zinc ions occupying the tetrahedral interstices. The coordination of the zinc and oxygen ions is seen to be with four ions that are oppositely charged. Due to the high polarity that zinc oxide exhibits, it favors the wurtzite structure rather than zinc-blende. The hexagonal wurtzite crystal structure of zinc oxide does not exhibit inversion symmetry which leads to certain properties such as strong piezoelectricity.

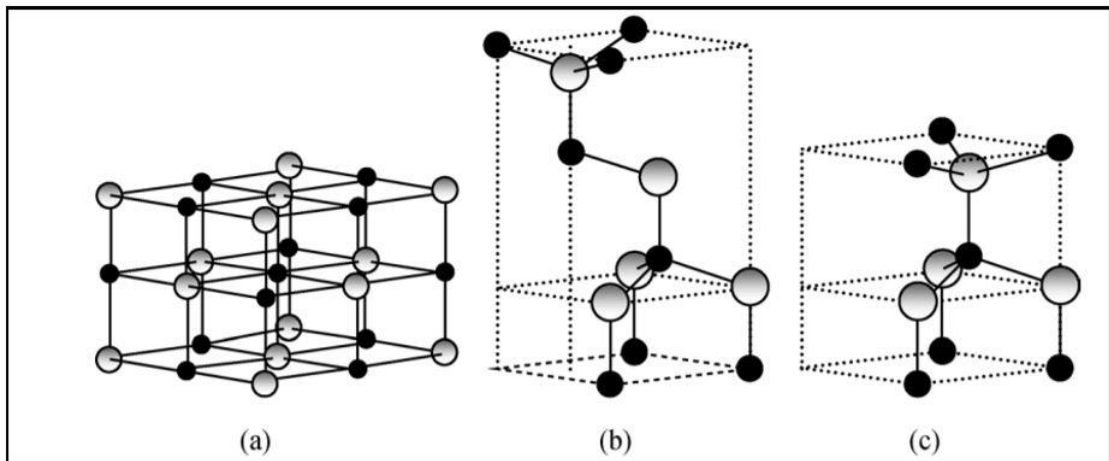


Figure 2.1 Several Zinc Oxide crystal structures where a) rocksalt, b) Zinc Blende and c) hexagonal wurtzite. To visually represent the elements, shaded black spheres were used as oxygen atom and grey spheres as zinc elements(2).

To fully understand the characteristics of zinc oxide, the crystal structure has been investigated intensely over the years. For instance, studying the lattice parameters of the compound provides researchers with critical information about its thermal properties, defects present, as well as compositions of solid solutions, which is achieved by conducting X-ray diffraction [6]. Zinc Oxide is described as a technological material, meaning that it has the potential to contribute to drastic changes and results. For instance, when studying the wurtzite structure of zinc oxide, it was found that there is no center of symmetry. Combining this with its large electromechanical coupling factor, zinc oxide exhibits strong piezoelectric properties.

Because of the wide range of properties that zinc oxide exhibits, it becomes of such importance and significance in research and device applications and allows for its growth to happen in multiple aspects. This is because when a material exhibits a large bandgap, it becomes more useful since the range of working temperatures is higher, higher breakdown voltages are produced as well as being able to maintain high electric fields. Zinc oxide (ZnO) is used for the unique properties that it has as well as its being under the group of nanostructures that are desirable to work with when properties and structures are studied. The research was conducted to evaluate and compare the behavior of zinc oxide bulk crystals with the nanostructures and it was found that the nanostructures are chemically and thermally more stable. ZnO also features spectacular stability in terms of n-type semiconducting

materials giving it the advantage to be used in a vast number of applications including solar cells, super capacitors, and biosensors piezoelectrics. Nanostructures are more favorable than bulk structures due to the range of methods that can be used to grow them [7]. There are a variety of ZnO nanostructures, however nanorods and nanowires are the two types that have attracted the most attention. The reason for this is that ZnO nanostructures exhibit certain properties that can be used to control the size and dimension.

2.2 GENERAL CHARACTERISTICS OF NANOWIRES

Materials are known to exhibit different properties and behaviors when their physical size starts to approach the nanoscale. The behavior seen in this scale tends to be distinct and in contrast with their traditional behaviors. Researchers studying and understanding these behaviors display the potential that the nanoscale can have, especially in electronics. Nanowires typically exhibit diameters that are equal to or less than 100 nanometers and can be made of a range of materials. Some of the features that differentiate nanostructures such as nanowires from other structures are their properties such as large specific area, high sensitivity, and isoelectric points as well as good compatibility. Among these nanostructures, semiconductors that exhibit a nanowire shape are distinctive from other nanostructures in their behavior, mainly because their bandgap can be easily influenced when stoichiometry is changed. For instance, the mechanical properties, specifically the flexibility of the materials, will change allowing it to be flexible. The reason for such behavioral change is because the chemical potential at the surface of the nanowires is higher than that of bulk materials, allowing for properties such as electrical, optical, magnetic, and mechanical properties to enhance [8].

The different types of nanostructured materials are centered on the synthesis method used to prepare them. There are four main types of nanostructured materials, classified according to dimensions, known as zero-dimensional (0D), one-dimensional (1D), two-dimensional (2D), and three-dimensional (3D) nanomaterials. Zero-dimensional nanomaterials such as quantum dots and upconversion nanoparticles (UCNPs) have shown to be beneficial in areas that include disease diagnosis and ion detection due to their extremely small size [9]. An example of zero-dimensional nanostructures is graphene quantum dots which can control the

photoluminescence excitation and emission wavelengths by controlling the dimensions. One-dimensional nanostructures including nanowires, nanotubes, and nanorods, have recently become a new focus in research due to their distinctive application uses especially in nanoscale devices. Depending on the functionality, one-dimensional structures can be applied in both forms, either as interconnects or as functional units in the device being fabricated. Synthesizing one-dimensional nanostructures with well-controlled characteristics such as dimension, morphology, and chemical composition can be achieved by two necessary steps: nucleation and growth. With the increase in the concentration of the solid, nuclei begin to form in a process known as homogenous nucleation which later turns into the seeds for the growing process [10]. Two-dimensional nanostructures portray a layered structure allowing it to have a strong bond in-plane and in between the layers, there are weak van der Waals bonds. For this reason, they are distinct by their physical properties such as having high Young Modulus and strength. A well-known example of two-dimensional nanostructures that is widely used in many applications is graphene [11]. Three-dimensional nanomaterials are considered to be different than the others because they are not restricted to the nanoscale dimension. The differences between their structures are shown in Figure 2.2.

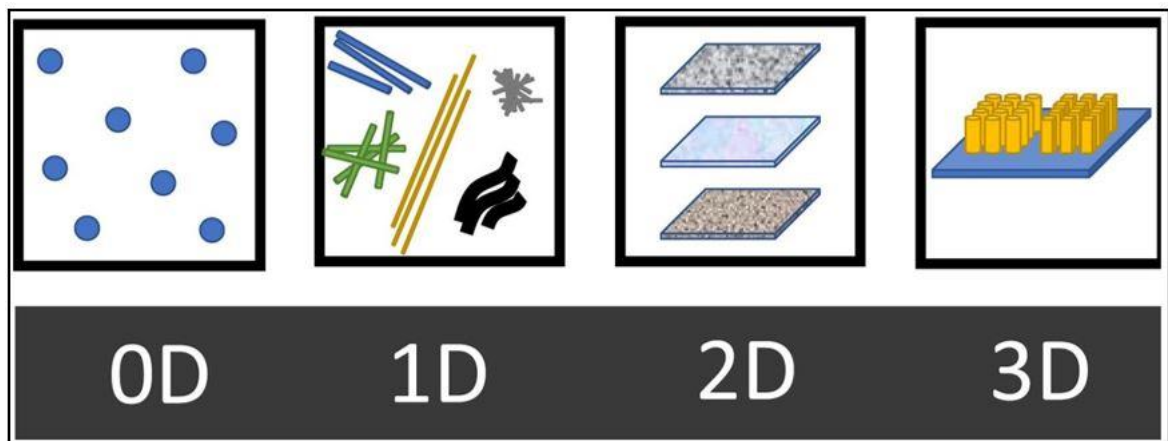


Figure 2.2 Zero-dimensional, one-dimensional, two-dimensional, and three-dimensional nanomaterials (3).

Manipulating and controlling the properties of the materials at a nanoscale or to certain levels such as the localization length or Bohr's radius allows them to exhibit certain behaviors,

different than their conventional behavior. Understanding the nanowire structures in some cases such as the quasi-1D allows for exploring their probable use in electronics. Another property that distinguishes the nanowires from other structures is the force required to cause mechanical deformation is much lower when compared with other nano-dimensional forms. What this essentially means is that when any type of stress, such as body motion, is caused onto the nanowires, the piezoelectric potential is generated onto them.

2.2.1 Zinc Oxide Nanowires

Zinc oxide nanowires are produced onto zinc oxide seed layers and can be done using a variety of techniques, each technique resulting in different structures. The shape of the nanowires, as well as the morphology, strongly depend on the different conditions used such as solution concentration, working temperatures, growth duration, and seed layer features (4). Based on the previous studies conducted, the concentration of the solution is directly linked with the shape and diameter of the ZnO nanowire produced and has the most effect. However, in terms of the length and size of the ZnO nanowires, they depend on the growth time where it was found that with the increase of the growth duration, the size and length also increased in a study was conducted by Chebil et. al. Figure 2.3 below shows some SEM images of different ZnO nanowires (5).0

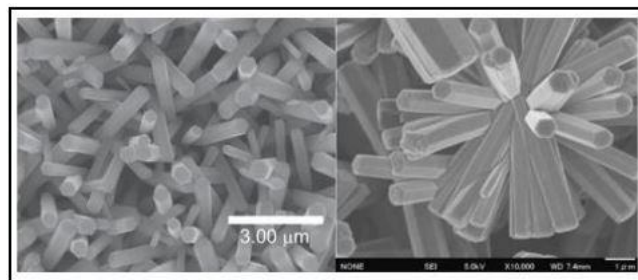


Figure 2.3 SEM images of (a) prism and (b) flower-like ZnO nanowires (5).

In terms of the XRD patterns conducted for the ZnO nanowires, it was found to be a wurtzite hexagonal structure. A variety of peaks can be seen in the XRD pattern but the sharpest peak, (002), correlates to the (0002) plane with a favorable orientation in the direction of (0001).

The typical X-ray diffraction pattern for zinc oxide nanowires can be seen in Figure 2.4 below.

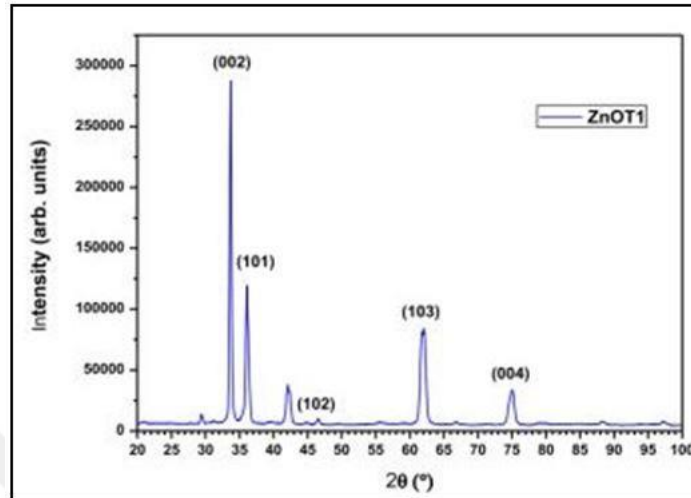


Figure 2.4 A typical XRD pattern for ZnO nanowires(2).

Along with morphological and structural properties of the zinc oxide nanowires, the optical properties have been investigated and typically include studying the transmittance, reflectance, and absorbance behaviors of the nanowires when present on a surface. Certain properties of the nanowires influence these behaviors some of which include aspect ratio, length, and diameter. With regards to the literature studied, it has been found that the transmittance of the ZnO nanowires will decrease as the nanowire grows longer. The transmittance values have been found to typically range between 65 and 90 percent where the difference is based on the synthesis technique used. This also impacts the electrical properties of the nanowires but the range of electrical resistivity has been found between $2.5 \times 10^{-4} \Omega$ and $3.5 \times 10^{-1} \Omega\text{m}$ (6).

Zinc oxide nanowires showcase a stable wurtzite crystal structure that can be thought of as two hexagonal closely packed lattices incorporating both zinc and oxygen atoms. These nanowires can be described as single-crystalline nanowires with the possibility to be synthesized in a variety of manners. Zinc oxide can be described as n-type doped meaning that the defects already present such as zinc interstitials or oxygen vacancies become electron donors. This causes the formation of donor levels but at lower levels. These defects also effect on the transport and optical properties of these nanowires (4). Zinc oxide nanowires can also be modified by using certain growth techniques. For instance, Liu et. Al proposed

the idea of fabricating zinc oxide nanowires as well as having intramolecular p-n junctions inserted into the anodic aluminum oxide (AAO) templates, a template allowing for consistent porous structures and diameters of a certain thickness. When conducting electrical measurements for these nanowires, it was found to align with those collected from a single ZnO nanowire. This is of such importance because it allows for the range of applications for these ZnO nanowires to increase(7). Apart from this, ZnO nanostructures offer many advantages, one being their high surface-to-volume ratio. Due to this, ZnO nanostructures become suitable for use in the field of energy conversion. With regards to the mechanical and electromechanical properties, zinc oxide nanowires have been inspected as essential components for nano-piezotronics. This is a new area in technology where nano-devices that are self-powered can harness their energy by using piezoelectric nanostructures(8).

2.3. GROWTH METHODS OF ZINC OXIDE NANOWIRES

The growth of nanowires is dependent on the direction and due to the crystal structure that ZnO exhibits, the growth can take place. To explain the phenomena of the importance of the crystal structure, the basal plane (0 0 1) is important. On each side of the basal polar plane, there is one terminating Zn lattice points that are partially positive and the other terminating Zn lattice point that is partially negative. Along the c-axis [0 0 0 2] direction the growth of these nanowires takes place (9). There are a variety of methods to synthesize ZnO nanowires, some of which are described below. The growth techniques differ in their costs and conditions needed. It has been found that all techniques apart from vapor-liquid-solid growth, hydrothermal growth, and solution-based growth methods are categorized as costly and high in expense mainly due to the operating temperatures that are needed.

2.3.1. Template Assisted Growth

Template-assisted growth can be seen as the easier synthesis method to grow nanowires. This is because in this method, small-sized holes that are cylindrically shaped are found in

the template and this is where the nanowires are grown and take the shape. The uniqueness of this method is that it allows for the use of any material to synthesize nanowires(10). The common technology known as lithography is usually used to produce these templates. In a study conducted by Canlin O. et al. (2016), the successful fabrication of a flexible and robust piezoelectric nanogenerator on a polymer-ceramic nanocomposite structure was established by using template-assisted hydrothermal synthesis(11). This was done by using nanoporous polycarbonate (PC) template that allowed for uniform and dense zinc oxide nanowires to vertically grow. These ZnO nanowires portrayed a high aspect ratio (diameter and length around 250 nm and 12 μm , respectively) and 4.2 percent energy conversion efficiency. The fabrication process begins with the pretreatment of the nanoporous polycarbonate template (pore diameter 200 nm, length 12 μm , and 12 percent porosity) with 1 M hydrochloric acid to allow for the pores to open. The hydrothermal synthesis occurred in two steps: first, the templates were seeded with ZnO nanoparticles into the pores by immersion in the precursor solution that consists of 50 mM zinc nitrate and 25 mM hexamethylenetetramine (HMTA) and is subsequently heated at 95°C for two hours. The templates were removed and gently washed with hydrochloric acid (HCl), removing the ZnO crystals deposited on the surface of the templates. Before the nanowire growth, the seeded PC template was vacuum-treated to remove all the air trapped inside the pores. The template is taken and immersed into a Teflon-sealed stainless steel autoclave reactor with half of its volume filled up with the precursor solution that consists of 50 mM zinc nitrate and 25 mM of HMTA. The hydrothermal synthesis was then performed at 95°C for five hours. Upon completion of the reaction, the templates were again gently washed with HCl. To refresh the precursor solution, the previous treatments on the PC template were conducted.

When conducting SEM analyzes, a dense array of vertically aligned ZnO nanowires of uniform length, grew within the confinement of the template. The average length of the free-standing nanowires was found as $8.4 \pm 2.1 \mu\text{m}$ and the ZnO nanowires grown within the PC templates show a higher aspect ratio compared to those grown from the same precursor solution directly onto ITO-coated substrates, where typical length is 4 μm . XRD analysis shows that only the PC templates filled with ZnO nanowires show the formation of a dominant peak from (100). Having higher-order peaks suggests that these nanowires are polycrystalline. This method is one of the ways to synthesize well-aligned zinc oxide nanowires that show uniformity in length and diameter however the difficulty comes in

controlling this process. There are other forms of this type of growth that are dictated by what is needed to be produced. ZnO nanowires follow a functional mechanism for collecting energy that is based on the semiconducting and piezoelectric properties coming together. This permits the use of non-classical preparation methods of semiconducting nanowires such as electrochemical deposition. Nooshin et. al proposed a template-assisted method for growing zinc oxide nanowires via electrochemical deposition(12). Commercially available membranes with 0.2 μm pore size were used as the template for the growth. In this reaction, the gradual increase of the pH level was what induced the formation of the zinc oxide. As seen in the SEM image in Figure 2.5 below, the zinc oxide nanowires show vertical alignment with an equal radius for the majority of the wires.

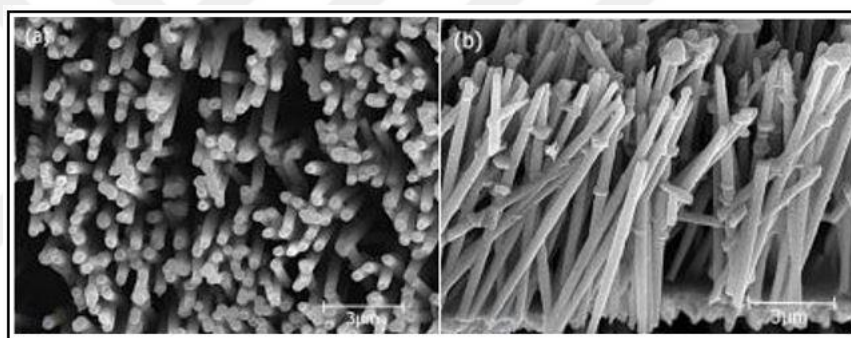


Figure 2.5 SEM analysis of ZnO nanowires vertically aligned grown by template-assisted method using 50 mM zinc nitrate solution with (a) top view and (b) cross-sectional view (12).

2.3.2. Vapor Phase Growth

This type of growth can be separated into two different groups: vapor-liquid-solid growth and vapor-solid growth. The vapor-liquid-solid growth method is usually used to grow nanowires because this technique allows for the control of the nanowires to be easy allowing them to be crystalline defect-free nanowires. This is because the precursors used are in gas form. Numerous research groups use this type of synthesis for producing zinc oxide nanowires. Naziha J. reported a growth system to produce zinc oxide nanowires using silicon substrates as the base and initially adding a later ZnO buffer using thermal evaporation(13). Since time is an important factor when growing nanowires, a set of times was chosen to

range from zero, 30, 90, and 120 minutes at 650°C. With the use of x-ray diffraction analysis (XRD), field emission scanning electron microscopy (FESEM), and energy-dispersive X-rays, the zinc oxide nanowires were analyzed structurally, crystallinity, and morphologically. With the use of FESEM, it was found that that vapor-liquid-solid technique was followed and the ZnO buffer layer initially added acted like the nucleation site for the growth. The direction of the growth was proven to be in the c-axis when XRD analysis was conducted and an intense peak at (002) was located as well as a wurtzite structure. The schematic of the VLS growth mechanism for the zinc oxide nanowires is represented in Figure 2.6 below.

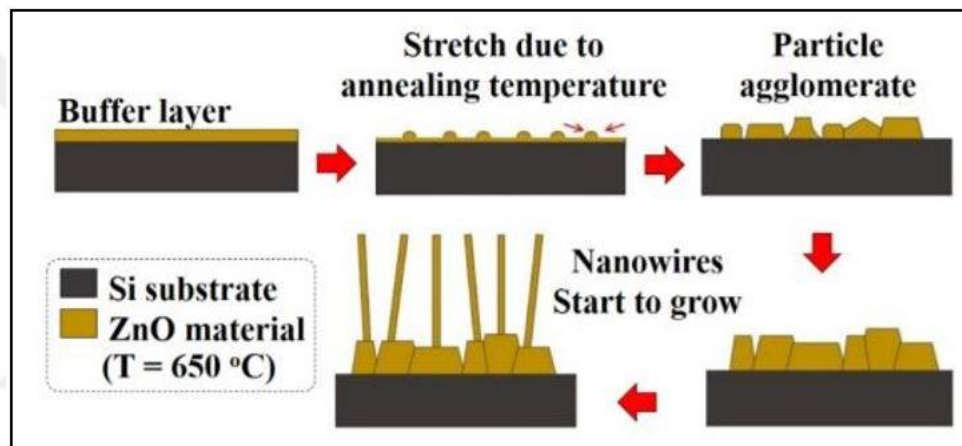


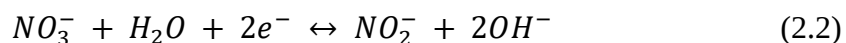
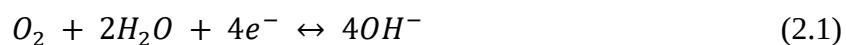
Figure 2.6 The schematics of the vapor-liquid-solid growth mechanisms for the zinc oxide nanowires grown onto the buffer layer(13).

Certain configurations need to be considered when using the VLS growth method. These features include lower activation energy for the growth to begin compared to the vapor-solid growth. The processing parameters such as metal catalyst layer thickness or deposition pressure, are important to consider when growing zinc oxide nanowires because these have a large impact on the quality of the nanowires produced. Unlike the VLS process and how it uses a metal catalyst, the vapor-solid process involved the direct nucleation of the gas phase onto the seed layer. This seed layer is made out of zinc oxide and is done so under controlled parameters such as temperature and pressure.

2.3.3. Electrodeposition

Electrochemical deposition is another synthesis technique that is used to produce uniform ZnO nanostructures in large areas. For this type of growth to take place, the availability of an intense external force is needed which leads to the reactions taking place, both spontaneous and non-spontaneous reactions. For this reason, ZnO nanostructures can grow on multiple substrate types, whether curved or flat, providing it is conductive (14). Compared to most of the growth techniques with the presence of such an external field, electrodeposition allows for greater substrate adhesion and higher quality alignment of the ZnO nanowires.

In terms of the setup needed for undergoing electrodeposition, three electrodes are needed, Ag/AgCl functioning as the reference electrode with the counter-electrode as Pt. The positioning of the anode is set to be alongside the deposition solution. Either a constant voltage or current source is used to control the electrical bias in this system and to sustain a constant reaction rate. This type of growth mechanism has proven to be one of the best in terms of doping of ZnO nanowires. In a study conducted by Zhao et. al, it was found that with the use of $\text{Zn}(\text{NO}_3)_2$ as a precursor, the reduction of NO_3^- will take place at the cathode causing a constant supply for OH^- ions(15). Under the process of dehydration, OH^- conforms with Zn^{2+} and results in the formation of ZnO. This can be seen in the four equations below.



Electrodeposition can be described as a cost-efficient method that can be operated at low temperatures. It is also seen as a valuable technique for producing ZnO nanowires with consideration of certain parameters such as the material used, pH of the solution, and applied force since they have a critical impact on the outcome(16). An example of ZnO nanowires growth on SnO_2 substrates using electrodeposition is shown in the SEM image below in Figure 2.7. It is important to point out that these nanowires are free-standing, meaning that no seed layer was deposited to facilitate their growth.

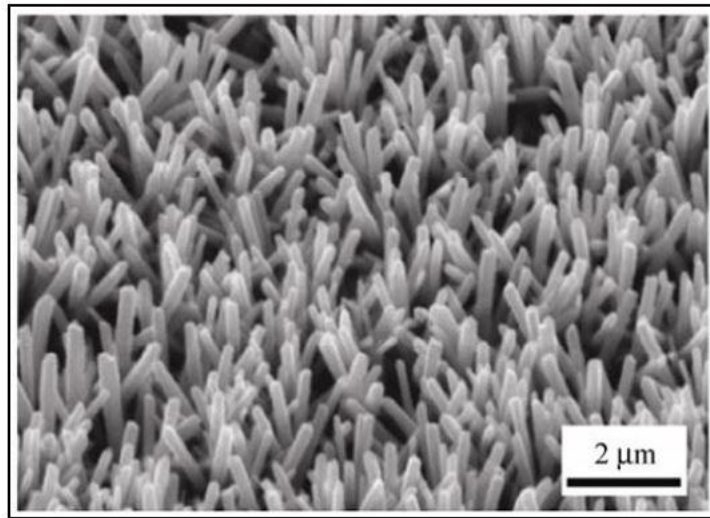


Figure 2.7 SEM image of ZnO nanowires on SnO₂ substrate by electrodeposition growth method(16).

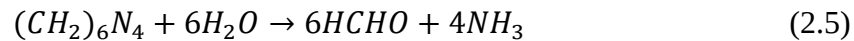
2.3.4. Solution Based Growth – Hydrothermal Growth Method

Along with vapor phase methods, another synthesis method used to produce ZnO nanowires is known as solution-based growth. However, unlike vapor phase growth, this synthesis has lower operating temperatures (growth) allowing it to become useful in a wider set of applications. This type of synthesis requires a solution and in the case that this solution is an aqueous solution it is described as the hydrothermal growth method. The electrochemical deposition method follows the principle of a thin layer of metal or oxide being deposited onto a substrate by what is known as the electrolysis process(17). This method can be described as using an external force to drive the reactions in order to grow zinc oxide nanowires that are uniform, especially over large areas without the need for a seed layer. The hydrothermal method has many benefits that distinguish it from other synthesis methods. Some of these include the ability to control the compositions of the nanomaterials synthesized by either following liquid phase or multiphase reactions. One of the key advantages of the hydrothermal method is the ability to synthesize nanomaterials that are not stable when the melting point is approached as well as it being a simple, low costing and environmentally friendly method (18). In the electronics applications specifically, this

method becomes of wide interest as it allows for the nanostructures to be synthesized at low temperatures making it suitable for flexible plastic substrates.

The procedure for hydrothermal synthesis of vertically grown zinc oxide nanowires can be generalized into four parts. Initially, a thin layer, known as the seeding layer, of zinc nanoparticles is added onto a specific substrate, usually by spin coating. The importance of this layer is that it promotes or initiates the nucleation process for the growth of the nanowires since it results in the thermodynamic barriers being lowered. The following step includes a mixture of an aqueous solution of an alkaline reagent, for instance, hexamethylenetetramine (HMTA) or sodium hydroxide (NaOH), with a zinc salt to act as a precursor in the synthesis process. After setting the growth temperature and duration, the seeded substrates are placed into the growth solution. Finally, upon completion, the substrates are washed and dried, and characterized. In this method, four main chemical reactions take place which are decomposition reaction, hydroxyl supply reaction, supersaturation reaction and zinc oxide nanowire growth reaction, as stated below(19).

Decomposition reaction:



Hydroxyl Supply Reaction:



Super saturation reaction:



Zinc oxide Growth reaction:



Understanding these reactions and the significance of each one is important because they directly influence the properties and quality of the nanowires produced.

Researchers have shown a variety of methods to grow single-crystal zinc oxide nanowires, especially intense studies on the hydrothermal method. Demes T. et al. proposed a hydrothermal procedure to grow these single-crystal ZnO nanowires on sol-gel deposited seed layers(20). In the research conducted, Demes concluded that by collaborating and optimizing the most suitable parameters, those that include seed layer properties, growths of various time durations, and multi-growth processes, one can produce nanowires with characteristics ranging between 20 - 25 nm in diameter, 1.0 - 9.0 μm in length and 30 - 50 aspect ratios (21). The growth rates that the experimental model developed were to be around 0.01 nm/min in the lateral direction and 25 - 40 nm/min in the longitudinal growth. In the procedure of deposition of the ZnO film, a sol was prepared from 100 mL of zinc acetate dihydrate (ZAD) and hexamethylenetetramine (HMTA) with fixed concentrations of 25 mM for 20 minutes at a temperature of 90°C. The two ZnO-coated wafers were then submerged in a bath for durations varying between 45 minutes to 20 hours. To allow for multi-growth to take place, the bath was refreshed one to five times after each growth process was completed. The SEM images conducted revealed that the ZnO nanowires exhibited a variety of mean grain sizes and surface coverage rates. The growth that was seen showed uniform nanowire growth but wasn't entirely perfect in the vertical direction.

In terms of the growth kinetics that the zinc oxide nanowires follow, the main approach is linked to the concept of heterogeneous nucleation being more advantageous than homogenous nucleation. In the case of heterogeneous nucleation, the location of the nucleation is known to be on the grains or grain boundaries. This is due to the instability that is present at the grain boundaries. It can be said that the growth of the nanowires takes place on the pre-existing ZnO seeds because the supersaturation levels are lower than if it were to take place in the solution itself (22). The temperature of the medium is also known to influence on the growth kinetics of the ZnO nanowires. This is because as the temperature increases, the growth rate is found to also increase simultaneously.

2.3.4.1. Seed Layer

The importance of the seed layer is that the thermodynamic barriers become lower giving rise to nucleation to happen. This seed layer can be added onto the substrate by a variety of methods, including sputter deposition, physical vapor deposition, and spin coating. Researchers have focused on studying the characteristics of this layer while changing the parameters to find the best outcomes. This is because properties such as the density, thickness, and crystal size of the seeds directly impact the nanostructures grown (23). Upon completion of depositing the seed layer, the substrates must undergo a type of heat treatment known as annealing, in different atmospheres and argon plasma treatment. The reason for this is to enhance the adhesiveness of the nanoparticles with the surface of the substrate as well as improvement in the alignment of the growth so that it will potentially be more vertical and stand upwards as well as improve the crystalline structure of the ZnO nanowires. In a study, Greene L. et al. conducted studying the effect of different annealing temperatures of the seed layer(24). The temperatures ranged from 100 to 450°C showing a variety of results. The results presented were temperatures below 100°C was not suitable since no textured seeds were formed, between 150 and 200°C alignment took place, temperatures around 350°C resulted in the growth on nanowires and at more elevated temperature crystallinity and growth occurred leading to nanostructures such as nanorods. Y. et al. presented a study that investigated the different effects of heat treatments on the seed layer. Three different treatments were conducted: pure argon plasma treatment (50 W for one hour), annealing in argon (600°C for one hour), and annealing in oxygen (600°C for one hour). The XRD analysis in Figure 2.8 below shows the different intensity levels for each treatment environment. From this it was concluded that all the seeds were aligned in the c-axis direction, annealing in an oxygen or argon environment leads to an evident rise of the (002) diffraction peak's intensity level, and a subtle decrease in the peak's intensity with argon plasma treatment (25). This meant that at higher intensities, the grain sizes are larger and crystallinity is improved.

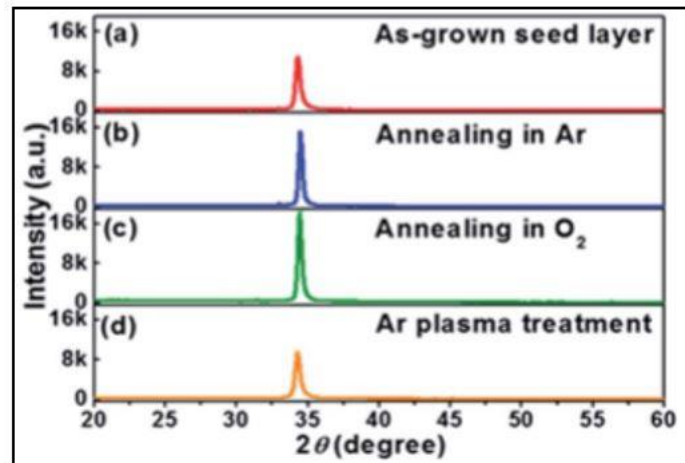


Figure 2.8 XRD analysis of (a) seed layer with no heat treatment, (b) annealed in argon environment, (c) annealed in oxygen environment, and (d) argon plasma treatment (26).

There have been many studies about the influence of the seed layer on the nanostructures formed. For instance, Ghayour et. al studied the impact of the seed layer thickness on the alignment, diameter, growth rate, and density of ZnO nanorods. Thicknesses of 20, 40, 160, and 320 nm were prepared on silicon wafers and the nanorods were then grown following the hydrothermal method, for 2 hours (27). In terms of the thickness of the seed layer, research has shown that increasing it leads to diameter increase, density decrease, and a faint decrease in the length of the nanorods grown. Along with the thickness, it has been found that the roughness and crystallinity of this layer have a significant effect on how the nanowires are aligned.

2.3.4.2. Growth Conditions

In the growth process of the zinc oxide nanowires, the predicted reaction to take place is known as hydrolysis and this happens when the zinc salts are formed with the use of either strong or weak alkalis. These reactions that take place can be described as reversible equilibrium reactions and are driven by minimizing the free energy in the system. To further explain the theory behind the formation of one-dimensional nanostructures in this solution, it can be said that when the ZnO nucleus begins to form, the precursor particles are absorbed onto the polar surfaces to create minimal energy. Some of the most common chemical reagents used in the growth of the zinc oxide nanowires are zinc nitrate hexahydrate and zinc

acetate dihydrate and HMTA combined in an aqueous solution where the O^{2-} ions come from the H_2O molecules. The importance of HMTA in this reaction is still not 100 percent clear but it is believed to behave similarly to Lewis's base for the present Zn^{2+} ions. Another significant effect of using HMTA is the facilitation of the growth direction to be in the [0001] direction.

The equilibrium state of the reactions taking place is controlled by the different parameters which include temperature, pH, and concentration of the growth solution as well as the growth time. These parameters each influence the produced nanowires in many ways. This can be linked to the crystallization theory, a process that involves the development of crystalline materials from either an amorphous solid, liquid, or gaseous material. The important aspects of this theory are identified as follows: the nucleation rate and the growth rate. Both of these factors strongly rely on the concentration of the solvent used. In some cases, after the main growth or saturation of the formation of crystalline material takes place, secondary nucleation may happen. In this case, the growth of crystals depends more on those already found. Other than the concentration of the solvent, other factors influence the growth of the nanowires, both in quantity and quality. For instance, the density of the ZnO nanowires can be determined by the concentration of the precursor used. On the other, different temperatures and growth times result in different morphologies and aspect ratios. The pH is also found to be an important factor that contributes majorly to the growth of zinc oxide nanowires. This is because it has an effect on the morphology of the nanowires and can range from nanoprisms and hexagonal nanowires to nanoflowers, depending on the pH value (28). As well as this, different temperatures were studied to acquire detailed information on the relationship between solution temperature and the growth of the nanowires. Chevalier-Cesar et. al hydrothermally grew ZnO nanowires for two hours and chose the solution temperatures as 60, 70, 80, and 90°C (29). The results showed that the minimum temperature of the growth medium should be 60°C to be able to produce nanowires and with increasing the temperatures, the length increased. The SEM images of the zinc oxide nanowires are presented below in Figure 2.9.

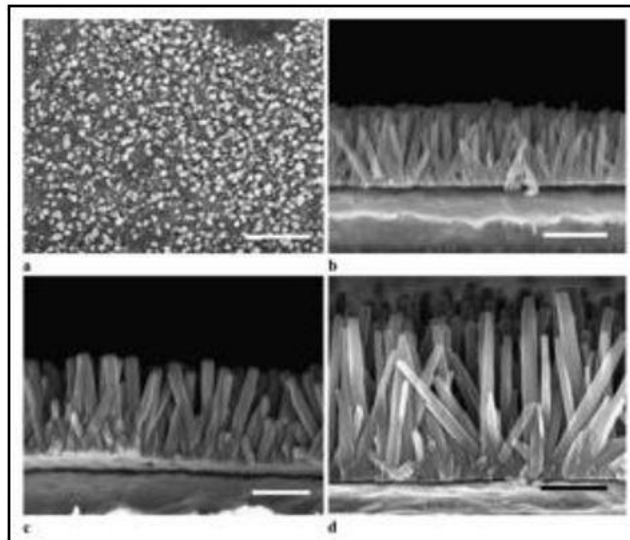


Figure 2.9 (Scale bar: 300 nm) SEM analysis of hydrothermally grown ZnO nanowires at different temperatures: (a) 60°C, (b) 70°C, (c) 80°C, and (d) 90°C, respectively(29).

2.4. TRANSPARENT CONDUCTING OXIDE (TCO) COATED SUBSTRATES

The substrates used for hydrothermally growing zinc oxide nanowires are important as they are the base that they grow on. Specifically transparent conductive oxides (TCO) substrates exhibit the qualities of being electrically conductive as well as visually transparent. Having this property increases the range of applications that can be deployed. These TCO are composed of metal oxides that are doped and generally made to have polycrystalline or amorphous microstructures. Transparent conducting oxides can be categorized as n-type conductors indicating that donating the electrons is the essential conduction method. Some of the areas in which these substrates can be used include thin-film photovoltaics, organic light emitting diodes, sensors and polymer-based electronics(30). For this reason, researchers are constantly trying to improve the performance of these substrates. However, some of the challenges still face include finding lower resistivities without affecting the transparency of the substrates. One of the most used and widely known TCO is indium tin oxide [In_2O_3 : Sn] coated glass substrates which are used in a variety of applications due to their transparency and conductivity. Based on the research conducted, it has been found that the electrical conductivity of the TCO materials is relatively high, around $10^2 - 1.2 \times 10^6$ (S), with the

absorption coefficient in the ultraviolet and visible light range being less than 10^4cm^{-1} . This conductivity of the n-type TCO thin films relies on the density of the electrons while in the conduction band as well as its mobility.

In terms of the production of these thermal conductive oxides, many factors are considered such as the accessibility of the raw materials as well as the expenses needed. To be able to produce highly advanced n-type semiconductor TCOs meeting the requirements of their characteristics, one of two main strategies is employed. The first approach that increases the density of the conducting electrons is known as the doping of TCOs with other elements. The alternative approach that researchers follow includes phase-segregated two binary systems, where the conductivity is increased without hindering the transparency of the TCOs. The usage of metallic ions as dopants can be done with the condition that with the replacement of the native metallic ion, there should be enough valences in the donor. This is important because the aim is to increase the conductivity of the TCOs but without restricting their transparency.

There are various applications for TCOs, some mentioned in this section. One of the main uses for this is the transparent surfaces and doors in the laboratories, specifically the cleanroom to ensure that there are no static charges built up. These materials are also needed in the aircraft and windshields as an agent to help defrosting process since they work in a more uniform and faster manner. The difference between these two applications is that laboratory surfaces can tolerate high resistance values while in the case of the windshields, they must convey low surface resistance. Another common usage of TCO films is to minimize the transmission of heat in the summer while still providing light transmission in the visible range. In these cases, the conductivity of these substrates is not as relevant and the focus is more on the infrared reflectivity. In the industry, this is beneficial because it allows for the reduction in costs for both heating in the winters and cooling in the summers.

2.4.1. Indium Tin Oxide (ITO) Coated Glass Substrates (ITO-GLASS)

Upon its first development, indium was initially deposited by the use of vacuum evaporation of In/Sn metals or by radiofrequency sputtering of metal In/Sn targets. With the developments in technology, the availability of new equipment such as the planar magnetron sputtering device allowed for successfully developing ITO layers by roll coating, reducing the production cost-effectively. The reactions that take place in this process were further investigated and it was found that in the process of coating, theoretically, the replacement of the Sn atom with the In atom allows for the formation of three s-like impurity bands where one of them overlays the conduction band of In_2O_3 . With the Fermi level present in this band, metal-like conductivity behavior is seen.

In the industry, ITO-coated glass substrates tend to have low resistivity values of around 10^{-4} $\Omega\text{-cm}$ and high transmittance (more than 80 percent). Multiple studies concluded that the processing temperature is important to the resulting crystal structure of the ITO produced. At higher deposition processing temperature, the ITO produced exhibited polycrystalline properties with resistivity values roughly $1\text{-}2 \times 10^{-4}$ $\Omega\text{-cm}$. On the other hand, running the deposition at lower processing temperatures revealed amorphous ITO structures with resistivity values near $5\text{-}6 \times 10^{-4}$ $\Omega\text{-cm}$ (31). This because a problem because when the resistivity values increase, the conductivity decreases in contrast. As well as the presence of electrical conductivity and optical transparency relies on certain characteristics of the material such as the atomic arrangements of the metal cation or the number of these arrangements in both oxide structures, crystalline and amorphous as well as the occurrence of defects. Indium tin oxide-coated glass substrates are also used in gas sensors where electrical conductivity is of high importance. Transparent conductive oxides have been used over the years in a wide range of everyday applications such as desktop screens or watches.

2.4.2. Indium Tin Oxide (ITO) Coated PET Substrates (ITO-PET)

High demand for the production of TCO relies on the flexibility feature. This is because having flexible displays and electronics allows for the developers to understand the importance of think film mechanical properties and what can be done with them. However, one of the issues that arise from using these PET substrates is their low tolerance for high operating temperatures. Reaching these high temperatures is essential as they initiate the material changes, due to the thermal expansion increasing and the decrease of thermal durability, in terms of their electrical and mechanical properties. Another issue that researchers encounter is the unmanageable electrical properties and with the addition of the ITO layer onto the PET substrates, this area is explored (32). The deposition environments are essential in controlling the characteristics of these ITO films. In research conducted by Jung et. al where a variety of deposition conditions were tested to further understand the characteristics, mainly electrical and mechanical durability, that the PET substrates exhibit (31). The results of this study revealed that the increase in the resistance values is a result of the development of micro defects (micro-cracks) as well as the separation (at a micro-scale) of the ITO films from the PET substrates.

2.5. APPLICATION OF ZINC OXIDE

Nanostructures have been widely used in many areas due to the unique behavior and properties that they exhibit at such a small scale. Depending on their structure, they are classified into three main groups: zero-dimensional, one-dimensional, and two-dimensional as explained in further detail above. One-dimensional structures stand out in both laboratory research and industry usage because of their outstanding potential. Zinc oxide nanowires have been widely used in the world of nanotechnology for studying aspects related to electrical dependence or how the mechanical properties change with the reduction in both size and dimensionality. The nanowires play an important role in many areas such as chemical and biochemical sensors, optoelectronic devices, solar cells, and so on (33). Some of the applications of these zinc oxide nanowires are explained below.

2.5.1. Sensors

One of the earliest oxides to be used in gas sensing is zinc oxide because it can function as a gas-sensitive material. The reason behind this is the drastic effect of the absorption of gas molecules on their conductivity. As well as the range of gasses that are detectable by zinc oxide nanowires is large including CO, NO, H₂, NH₃, and O₂. These types of sensors are important in the real world because they allow for the detection of hazardous gases and vapors (34). In a study conducted by Chin-Guo et. al, an organic-inorganic semiconductor gas sensor was fabricated to detect ammonia gas (35). The inorganic semiconductor was composed of a ZnO nanowire array combined with the organic material poly(3-hexylthiophene) was predicted to portray enhanced electrical properties as well as the higher performance of the gas sensor. The sensing device can be seen in Figure 2.10 below. These types of sensors are critical to have since they are also able to detect different volatile compounds, which are organic, such as acetone, methanol, and benzene while other gasses require very sensitive measurements (parts-per-million, ppm) because they exhibit high toxicity effects. Because of the zinc oxide nanowire's functionality and working principle, it is possible to use them in resistive or conductometric sensors (36). Upon contact of the gaseous molecules with the ZnO nanowires and absorption is initiated, the resistance begins to change resulting in modifications in the surface. To be able to measure the current, a potential difference is employed through the electrodes, and using DC circuits, it is possible to measure the resistance change. The simplicity of this setup and measurements allows it to be widely used in many areas.

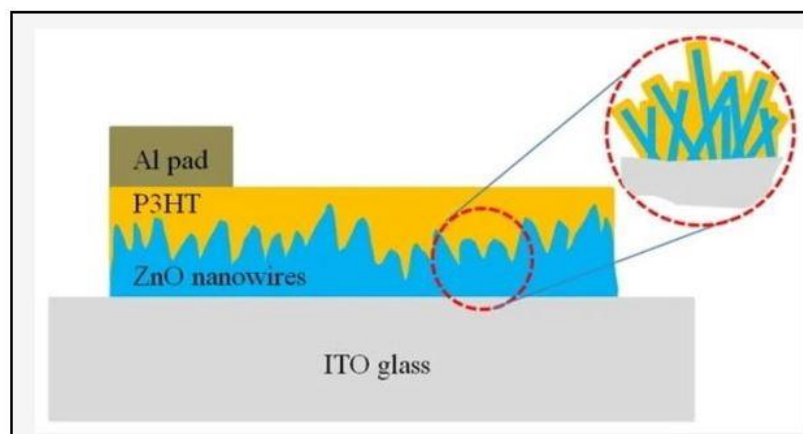


Figure 2.10 Diagram of the ammonia gas sensing device (35).

Due to its characteristics of it being low toxicity, bio-safe, interaction with immobilized enzymes, and biocompatible, zinc oxide nanostructures are implemented in many biosensor applications. An example of this is seen in a glucose biosensor fabricated by Liu et. al where ZnO nanorods films were physically grown on the ITO glass surfaces. The range of detection was found to be large starting from 5 μM up to 300 μM with high selectivity of glucose(37). There are plenty of biosensors fabricated, each serving different purposes and detections.

2.5.2. UV Detectors

Another optical application for ZnO nanowires is known as ultraviolet (UV) detection. In this case, the detectors rely on the electrical potential that the ZnO nanowires exhibit when UV irradiation takes place. One of the unique advantages that come with fabricating ZnO-based UV detectors and using such devices is that they are unaffected by the visible light signifying that they can be used for visible-blind detection with no need to add filters(38). Choosing ZnO nanowires for UV-photodetectors is more advantageous because the direction of their growth is controllable. A large number of UV-detectors have been fabricated using ZnO nanowires.

2.5.3. Photocatalysts

Recently, zinc oxide nanowires are implanted into photocatalysts for various purposes such as immobilizing viruses and bacteria or deterioration of environmental pollutants when there is suitable light present. Such processes are important because they contribute to environmental protection. By undergoing the process of photocatalysis, organic pollutants, with low concentrations, are oxidized to what are known as benign products which help protect the environment from hazardous products. The significance of using semiconductor photocatalysts is that they allow for a photo-induced oxidation process to take place in the action of breaking down these pollutants. The use of zinc oxide as the semiconductor has proven to show higher efficiency rates of both separation and generation of photo-induced electrons and holes. Since nanowires have a large surface-to-volume ratio, the photocatalytic efficiency is enhanced when comparing it to surfaces with no dimension (39). It is important to improve the photocatalytic activity of the materials which can be done by advancing the charge separation among the charge carriers. Conductive layers are deposited onto substrates to allow for this enhancing this behavior and with the use of ultraviolet-visible spectroscopy characterization technique, the color concentration can be measured (39).

3. EXPERIMENTAL PROCEDURE

This section explains in detail the experimental setup and procedure in order to be able to conduct the goals of this research. It also includes the different characterization techniques that are used to gather the results.

3.1. EXPERIMENTAL DETAILS

The growth of well-aligned zinc oxide nanowires that are of high quality requires the surface of the substrate to be carefully and properly cleaned of any contaminants present. This is because the presence of slight contamination will disturb the growth and formation of the nanowires. For this reason, the first step of this procedure was to clean the indium tin oxide (ITO) coated glass and PET substrates with acetone (99.8 percent pure), 1-isopropanol (99.8 percent pure) and distilled water by using an ultrasonic bath, each for 10 minutes respectively. To ensure minimal contamination, these substrates were dried with nitrogen flow after the cleaning process was complete. The ITO coated substrates, both PET and glass, were purchased from Technological Materials Industrial and Trading Incorporation. The chemicals used to conduct this experiment were all retained from Sigma-Aldrich and utilized as is without the need to purify them. To simply describe the growth process of the zinc oxide nanowires, it is known as a two-step process where the first step begins with the depositing of a seed layer on the substrate and then their growth inside a solution.

At first using the deposition method of spin coating, a 5 mM zinc acetate dihydrate solution mixed with 1-propanol was deposited onto the glass and PET substrates. This is known as the deposition of the ZnO seed layer. Based on the literature research conducted, the speed was set to 2000 rpm for 1 minute. This step was repeated as many times as desired to produce substrates with one, three, five, and 10 ZnO seed layers, where between each layer the substrate is placed onto a hot plate (90°C) for 45-60 seconds. This is to ensure that the deposited layer dries before the addition of the other one. Upon completion, the glass substrates with the ZnO seed layer undergo heat treatment, known as annealing, at 350°C for 20 minutes inside an oven. On the other hand, the annealing temperature of the PET substrates was set to 180°C for 20 minutes, based on the literature survey conducted. The number of times this is conducted depends on the desired density of the nanowires. The ITO

coated substrates (both glass and PET) with ZnO seed layer are then immersed into an equimolar aqueous solution, with a concentration of 20 mM, composed of zinc acetate dihydrate ($\text{Zn}(\text{O}_2\text{CCH}_3)_2(\text{H}_2\text{O})_2$) and hexamethylenetetramine (HMTA) in DI water. The solution in the beaker was clipped onto a support stand using a lab clamp while submerging three-quarters of it in an oil bath. The temperature of this oil bath is kept at an average of 90°C for various hours and it is very critical to place the samples into the solution once it comes up to the desired temperature. The time is the factor that determines the length of the nanowires so a variety of runs was conducted: 30, 60, 90, 180, and 300 minutes.

The chemistry that takes place for the nanowires to grow can be described as follows. Initially, the reaction between the HMTA and water takes place resulting in the formation of ammonium, known as the decomposition of hexamethylenetetramine(40). This ammonium then reacts with water yielding the formation of ammonium and hydroxide ions (hydroxyl supply reaction). As a result, the product reacts with the Zn^{2+} ions to initiate the formation of ZnO crystals, also known as the supersaturation reaction. Upon completion of the growth process, the substrates were taken out from the solution and washed with DI water followed by nitrogen gas for drying. This is important to ensure that there are no residuals left on the surface of the substrates. The spin coating device used for applying the seed layer onto the substrate is presented below in Figure 3.1 along with the experimental setup of the hydrothermal growth process.

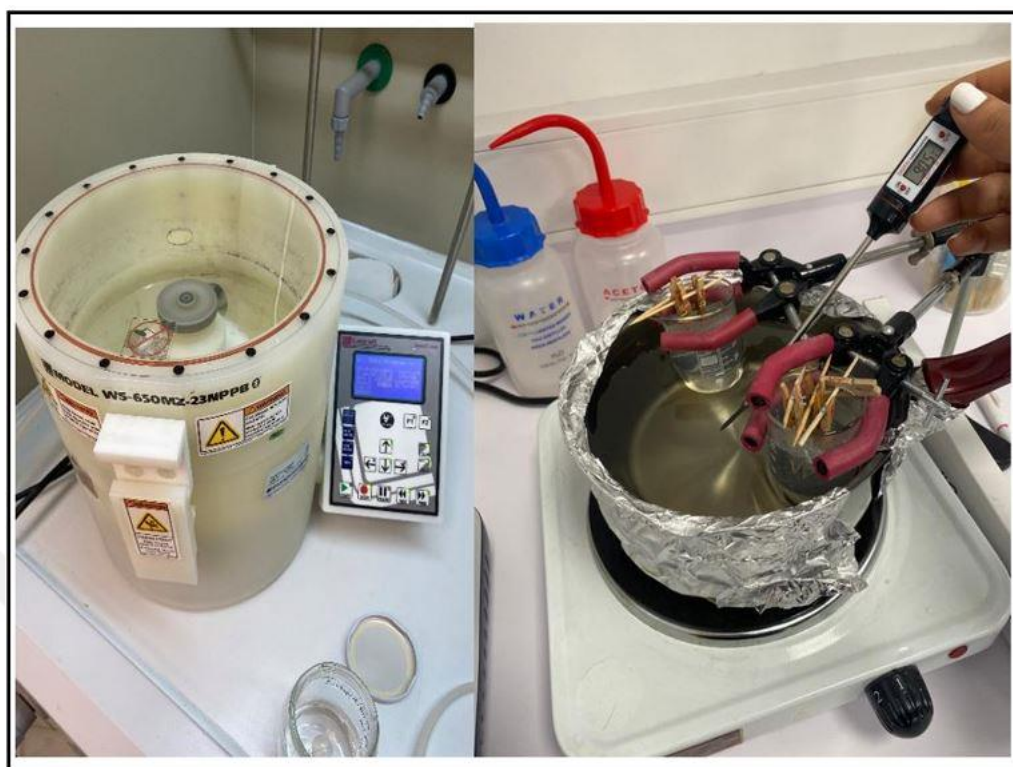


Figure 3.1 Spin coating machine and hydrothermal setup of the experiment.

The entire process can be summarized in the diagram presented in Figure 3.2 below. Initially, the seeding and growth solutions are prepared with the desired amounts and mixed until fully dissolved. After cleaning the ITO coated glass substrates, spin coating is performed to apply the seeding layers. To ensure better adhesion and growth of the nanowires, a heat treatment is applied known as annealing. According to the literature studied, it was found that 350°C for 20 minutes was the ideal time for the treatment (41). The next step is to place the samples in a 90°C oil bath and grow them for the desired time. According to the literature survey conducted, it was found that placing the samples after the desired temperature is reached, 90°C, will avoid having non-uniform growth of the nanowires. This was proven in a study conducted by Chevalier-Cesar et. al where he presented two different methods of growing nanowires. The first method was placing the seeded substrates into the growth solution at the desired temperature whereas the second method involved placing the seeded samples into the solution at room temperature and then gradually increasing the temperature (29). The results showed uniformly grown nanowires when the first method was used where they had narrow distribution. On the other hand, the second method resulted in cone-shaped

nanowires that had a wider diameter closer to the substrate. The final step to ensure no contaminants are found is to dry them in the oven for a few minutes and use nitrogen gas.

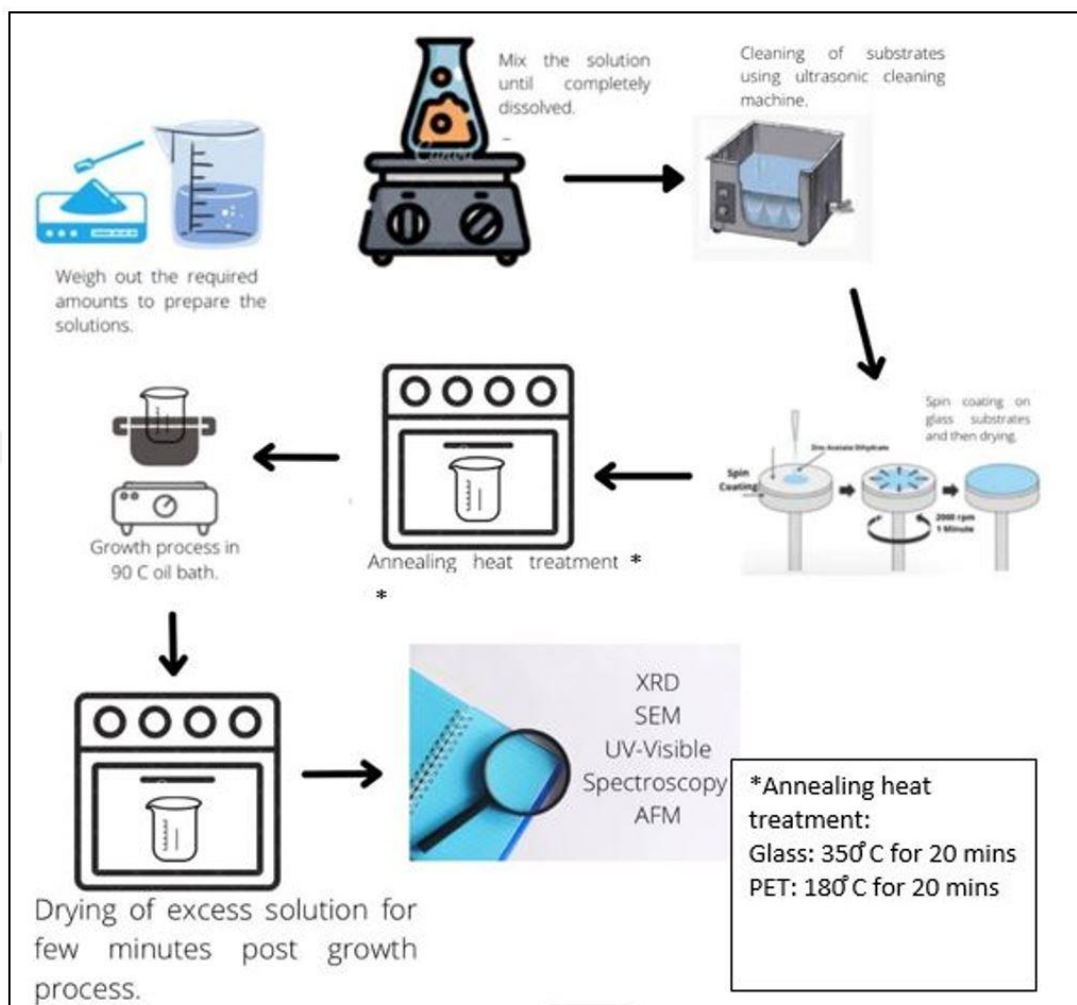


Figure 3.2 Experimental diagram of hydrothermal growth of ZnO nanowires.

3.2. CHARACTERIZATION METHODS OF ITO COATED SUBSTRATES AND ZNO NANOWIRES

3.3.1. XRD (X-Ray Diffraction)

The X-ray Diffraction analysis method is used for analyzing and understanding the crystal structure of both the indium tin oxide (ITO) glass substrates before and after the ZnO growth process. PANalytical X'Pert PRO MPD model XRD device, presented in Figure 3.3, was used to conduct this analysis. Input type of radiation used Cu-K α radiation ($\lambda=1.5406 \text{ \AA}$) at an X-Ray source operating voltage of 45 kV in the 2θ range between 20° and 70° at a scanning rate of $2^\circ/\text{min.}$) For the analyses of the growth samples. In terms of the ITO-coated pre-growth samples, the range was set between 2° and 70° with a step range of 0.02° . The XRD analysis was applied for all one, three, and five layers at the same settings to be able to compare them simultaneously.



Figure 3.3 X-Ray Diffraction analysis device.

3.3.2. SEM (Scanning Electron Microscopy)

The analysis of the ITO substrates before coating with the zinc seed layer and undergoing growth was done. To analyze the morphology of the zinc oxide nanowires as well as their size, Scanning Electron Microscopy (SEM) technique was used. Both the surface and the cross-section views for all layers were taken after coating them with platinum from TUBITAK MAM.

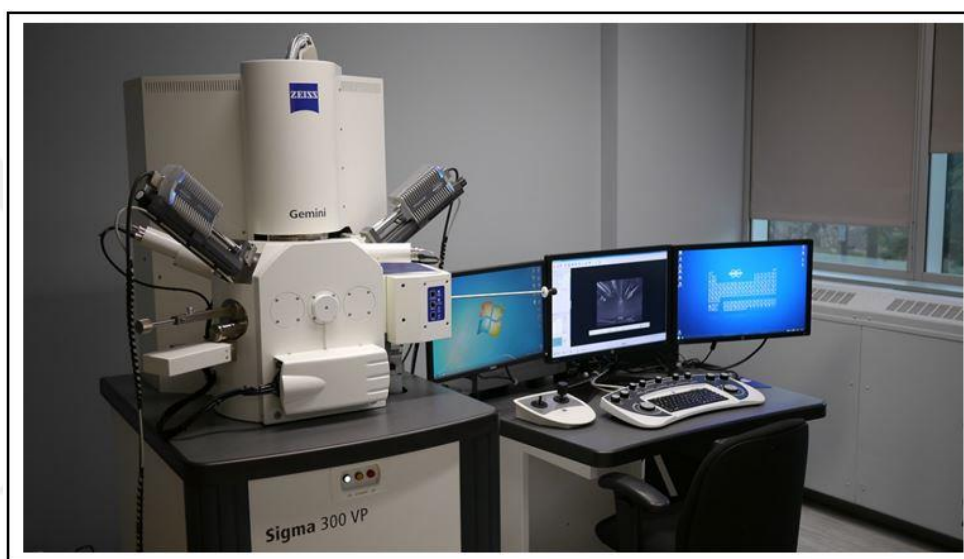


Figure 3.4 Scanning Electron Microscopy analysis device.

3.3.3. UV-VIS (Ultraviolet-visible Spectroscopy)

UV-Vis Spectroscopy characterization technique is used for measuring the absorbance level of the chemical substances to light considering the regions of ultraviolet and visible light. By using this device, a reference sample is first measured as a baseline then the light intensity of the light is measured for the coated substrate and compared to the reference. This analysis technique can be conducted for many sample types such as liquid, glass, or thin-films. PerkinElmer Precisely – Lambda 750S UV/VIS Spectrometer device was used operating at a spectrum of 2500 nm to 250 nm with an interval of 5 nm with ordinate mode set to transmission. This characterization technique enables researchers to analyze the behavior of the matter interacting with electromagnetic radiation or when emitting it. The device used to

conduct this analysis is presented in Figure 3.5 below, model, UV-Visible from TUBITAK MAM.



Figure 3.5 Ultra-violet-visible Spectroscopy (UV-VIS) analysis device.

3.3.4. AFM (Atomic Force Microscopy)

Atomic Force Microscopy (AFM) analysis technique is used to examine the surface topography of the substrates. This is important because it allows for the computation of the surface roughness numerically. Unlike the other characterization techniques, the AFM uses a non-optical surface interrogation approach where a physical probe comes in direct contact with the surface and measures its properties of the surface. There are three main features of this technique: topographic imaging, force measurements, and manipulation. For this study, topographic imaging is of importance as it portrays surface topography. Using Quesant Ambios Atomic Force Microscopy (AFM) Q-Scope-250 characterization tool from TUBITAK MAM, the analysis was conducted for the ZnO nanowires grown onto the ITO coated glass substrate. The analysis was done as a non-contact scanning type, with scan sizes of five, 10, and 20 μm , scanning rate of 1 Hz, and scan resolution of 300. The device used to conduct this analysis is presented in Figure 3.6 below.

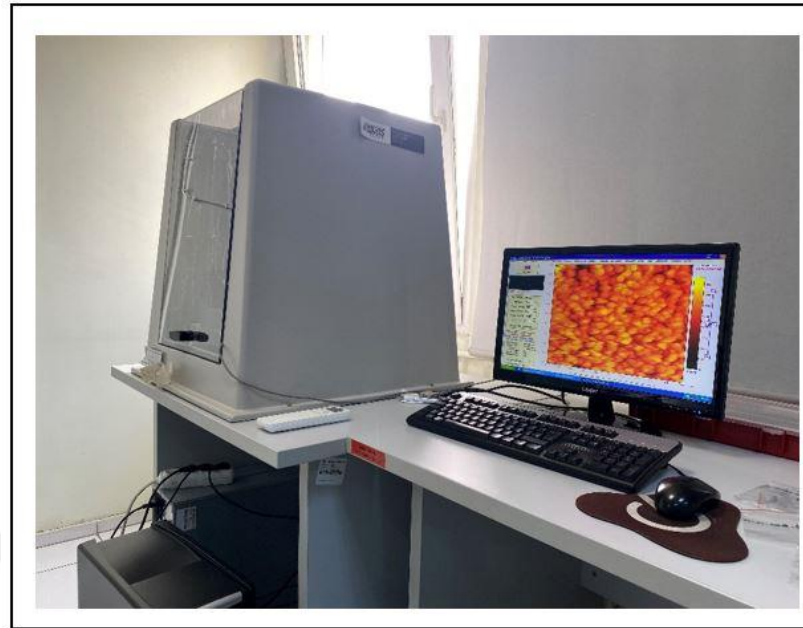


Figure 3.6 Atomic Force Microscopy (AFM) analysis device.

3.3.5. Electrical Conductivity Measurements

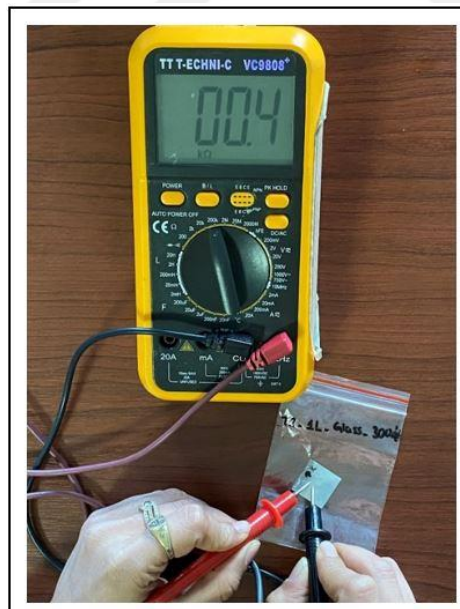


Figure 3.7 Voltmeter – Electrical measurement device.

4. RESULTS AND DISCUSSION

The results of multiple studies are presented below. First the results of the research conducted on the ITO-GLASS and ITO-PET substrates. Following this are the studies regarding the growth of the zinc oxide nanowires

4.1. CHARACTERIZATION RESULTS OF SUBSTRATES

4.3.1. ITO – GLASS

At first, the ITO coated substrates were investigated before adding the seed layer and growth layer and the results of the analysis are presented below. Six samples were tested, one with no ITO coating and five randomly selected ITO-coated samples out of 150 samples and three main characterization techniques were used: X-Ray Diffraction, Scanning Electron Microscopy, and Atomic Force Microscopy. The XRD diffractogram patterns for the six samples are presented in Figure 4.1 below. These graphs indicate that the composition of the elements present on the surface is the same, with minimal deviations. It is also clear that the samples have similar mineralogical content along with partial orientations. The ITO-coated layer on the glass substrates generally consisted of the In_2O_3 phase (ICDD Card No: 06-0416).

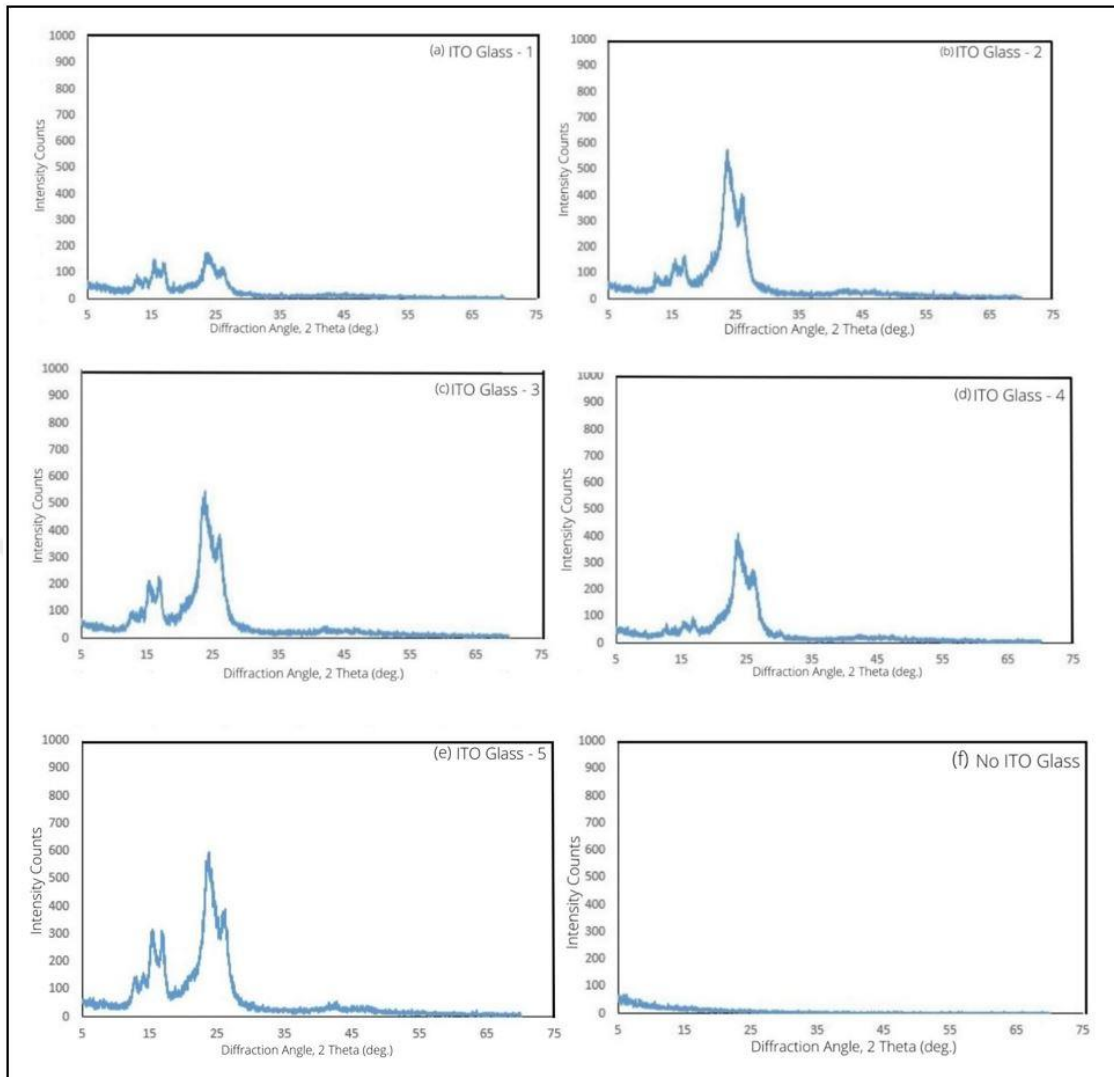


Figure 4.1 X-Ray Diffraction results of the five randomly selected ITO coated glass samples (a-e) and (f) non-coated glass sample.

With the use of the scanning electron microscopy characterization method, it is possible to analyze the homogeneity of the ITO coated thickness with a cross-sectional examination. The images are presented below in Figure 4.2 indicating the thickness values of each coating layer. The thicknesses of the ITO coatings varied between 186.6 – 224.4 nm with an average thickness coating of 207.5 ± 11 . With regards to this data, it can be concluded that no significant differences are present between the coating thicknesses of the ITO coated glass substrates.

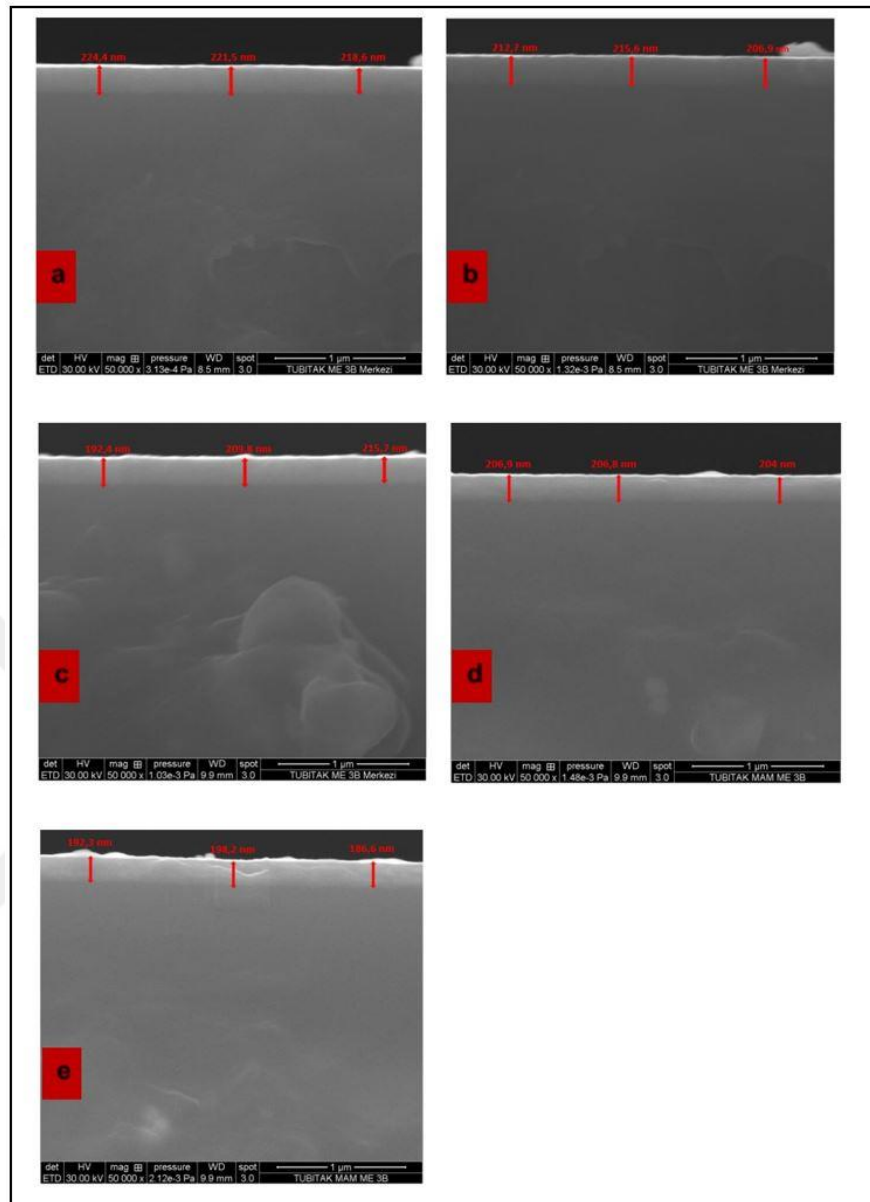


Figure 4.2 Cross-sectional SEM images of the ITO coated glass samples where a) 1, b) 2, c) 3, d) 4, and e) 5.

To further study and analyze the homogeneity of the ITO-coated surfaces, elemental mapping studies were carried out. This study is important because it allows for the identification of the elemental compositions of the sample areas as micron levels. According to Figure 4.3 presented below, the distribution of In, Sn, Si, Ca, and O elements is examined

on the thin films. It can be seen that the surface distributions of the elements are homogenous. From this, it can be concluded that the ITO coated glass can be used as a base in the ZnO nanowire growth.



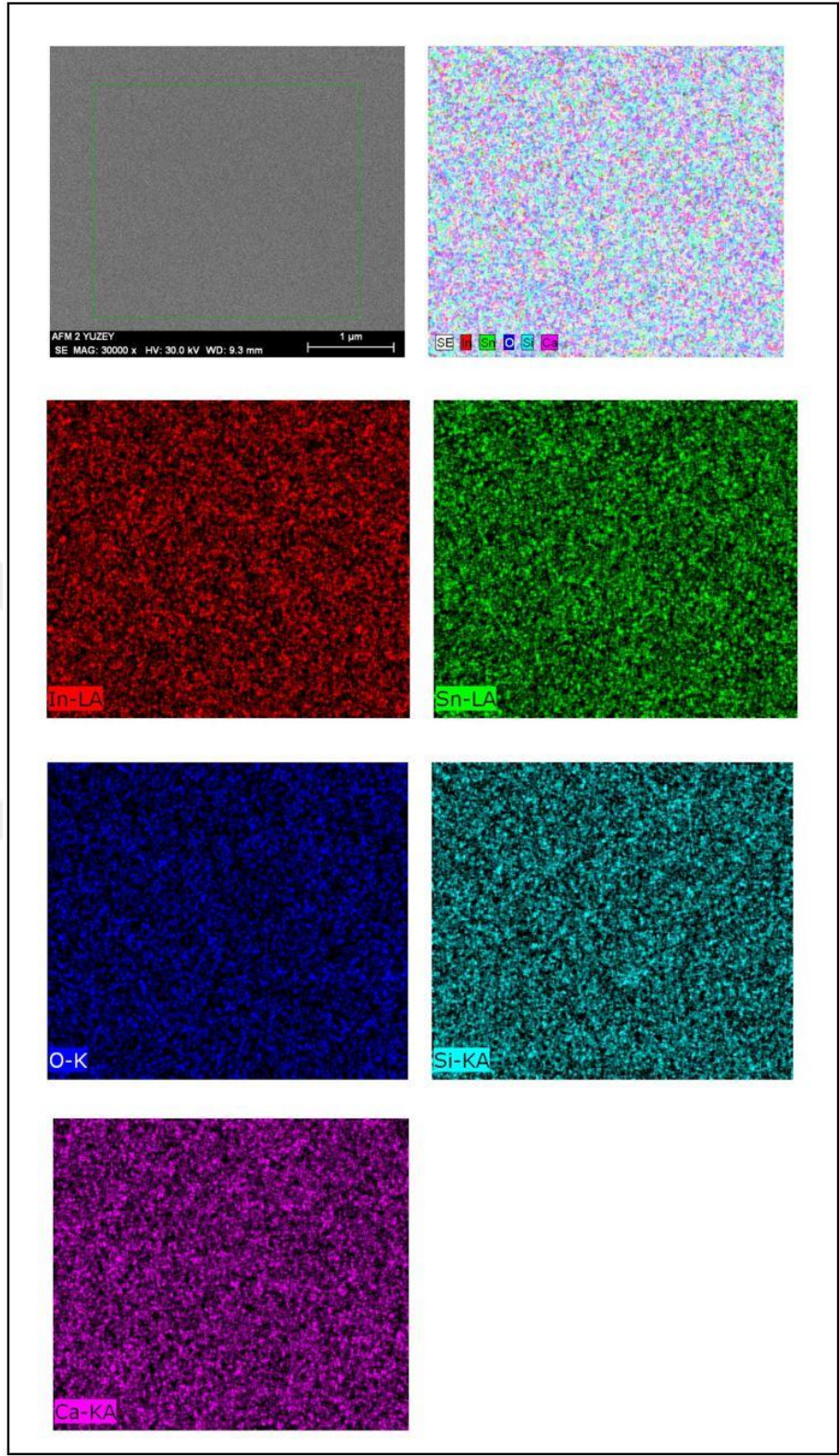


Figure 4.3 SEM and corresponding EDS elemental mapping images of In, Sn, Si, Ca and O elements for ITO coated glass.

To conduct surface roughness measurements on the indium tin oxide coated glass substrates, the atomic force microscopy (AFM) method was used. The size of the area measured was $40\text{ }\mu\text{m} \times 40\text{ }\mu\text{m}$ using the Quesant Ambios Atomic Force Microscopy (AFM) Q-Scope-250 characterization tool for both the coated and non-coated glass substrates. The measurements were conducted eight times and an average and standard deviation of the surface roughness was taken and is presented below in Table 4.1.

Table 4.1 Surface roughness measurements of ITO coated/non-coated glass substrates.

Number of samples	Surface Roughness [Ra, nm]
Non-coated surface	2.77 ± 0.97
1	3.17 ± 1.56
2	4.66 ± 1.38
3	2.95 ± 0.56
4	4.75 ± 1.71
5	3.98 ± 0.46

In order to portray the surface roughness measurement, the output is a surface roughness map which can be seen below for the six samples prepared in Figure 4.4.

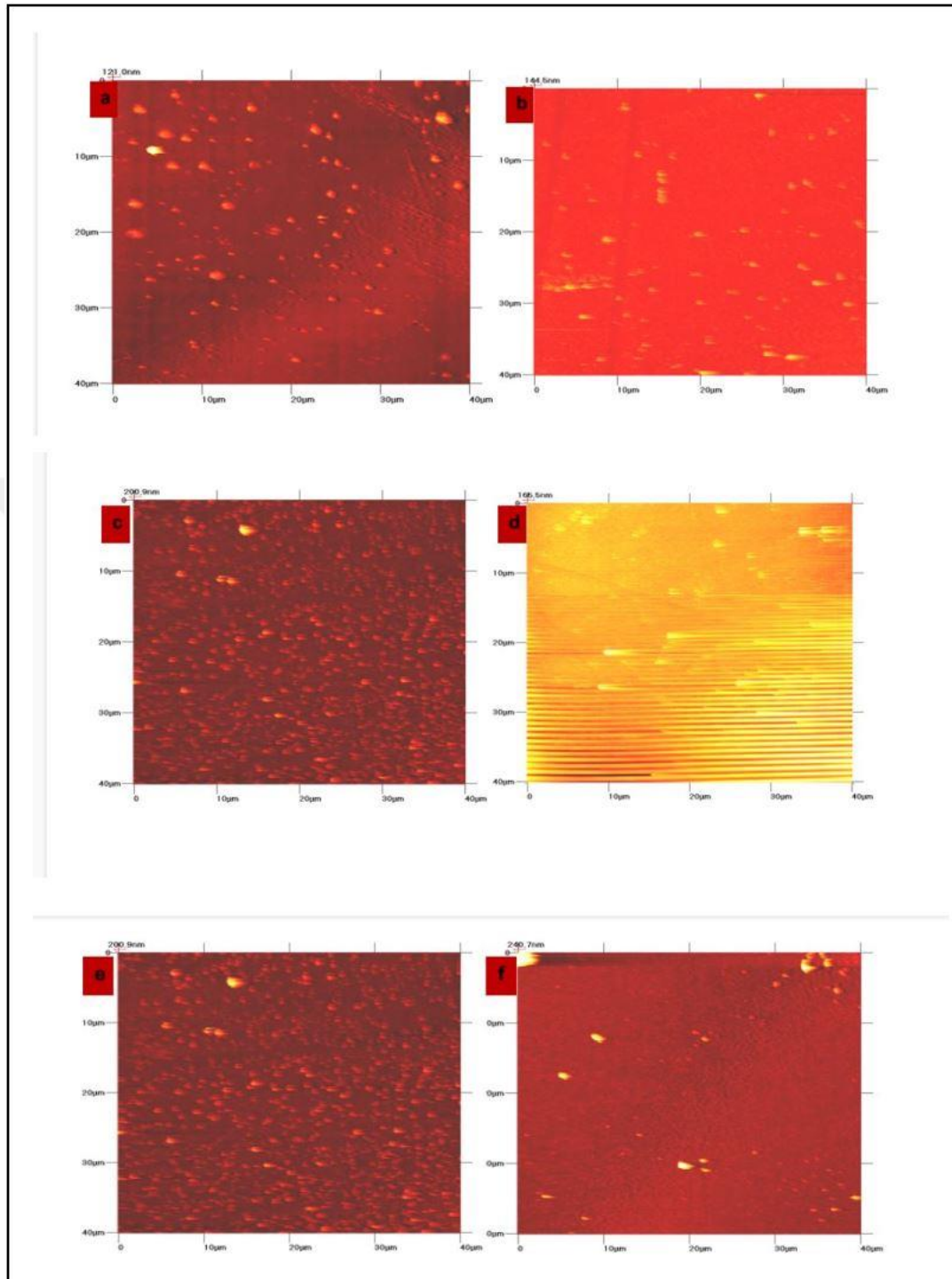


Figure 4.4 Surface roughness measurements of the ITO coated/non-coated glass substrates where (a) non-coated glass substrate, (b) 1, (c) 2, (d) 3, (e) 4, and (f) 5.

Alongside these studies, the surface resistance values for 10 different ITO-GLASS samples at five different places were studied before and after heat treatment to test if there are any significant changes. This is important because any change in the conditions of the electrode layer might disturb the growth process of the nanowires. The heat treatment was set to 200° C for two hours and the data is presented in Table 4.2 below.

Table 4.2 Resistance measurements of 10 ITO-coated glass substrates before and after heat treatment.

	Resistance values of ITO-coated glass before heat treatment (ohm)									
	1	2	3	4	5	6	7	8	9	10
	80	80	90	100	90	100	100	110	80	70
	90	90	60	110	80	70	90	120	100	90
	100	60	80	80	100	90	80	100	100	80
	70	100	70	90	100	80	70	90	60	80
	120	140	110	110	110	110	110	110	100	70
Average	92	94	82	98	96	90	90	106	88	78
	Resistance values of ITO-coated glass after heat treatment (ohm)									
	1	2	3	4	5	6	7	8	9	10
	80	80	90	80	80	100	80	90	90	80
	90	90	80	90	80	110	90	100	110	90
	110	90	80	100	90	110	100	100	110	90
	80	110	90	90	90	110	100	110	110	100
	90	100	90	100	80	130	70	120	110	100
Average	90	91	86	92	84	112	88	104	106	92

In order to further characterize the ITO-GLASS samples SEM analysis was conducted before and after heat treatment process. The results present that no cracks were observed on the ITO layer.

4.3.2. ITO – PET

The ITO-PET substrates purchased are also investigated in terms of surface resistance values before and after bending process and heat treatment. This was conducted due to the fact that cracks are present in the coating layers of ITO-coated PET substrates. Since these cracks increase in size post heat treatment and might have an effect on the growth behavior of the ZnO nanowires and conductivity of the electrode layer, it was important to investigate it further. Similar to ITO-coated glass substrates, the electrical resistance of 10 ITO-coated PET substrates was measured at five different places before and after performing a bending test and heat treatment. The bending test involved bending the ITO-PET substrates 100 times after conducting the heat treatment process of 100°C for two hours. The electrical resistance values are presented below in Table 4.3.

Table 4.3 Resistance measurements of 10 ITO-coated PET substrates before and after heat treatment and bending test.

	Resistance values of ITO-coated PET before heat treatment (ohm)									
	1	2	3	4	5	6	7	8	9	10
	140	100	130	110	3280	170	330	500	160	100
	200	110	100	100	3150	190	220	840	110	140
	400	120	150	80	3180	140	440	420	180	80
	820	150	200	120	3340	400	200	180	130	200
	170	160	80	160	3210	100	150	300	120	220
Average	346	128	132	114	3232	200	268	448	140	148
	Resistance values of ITO-coated PET before heat treatment (ohm)									
	1	2	3	4	5	6	7	8	9	10
	100	90	140	100	2250	130	260	1100	170	170
	180	170	100	130	2850	120	320	250	180	120
	250	220	200	140	3410	200	300	250	260	130
	210	180	210	130	3570	160	210	360	170	120
	280	120	240	90	3120	150	200	290	200	130
Average	204	156	178	118	3040	152	258	450	196	134

According to the table above, it can be seen that the resistance values are high before the bending test and heat treatment. It was observed that no significant changes after both processes. This is important since no defects were detected on the electrode layer meaning that no conductivity discontinuity is present. When comparing the resistance values of ITO-PET and ITO-GLASS after heat treatment, the values are lower in glass than those of PET. To further support these results, SEM surface images of the samples pre- and post-heat treatment are conducted for more sensitive analysis. The images of two randomly selected ITO-PET samples before and after the heat treatment and bending test (100 times) are presented below in Figure 4.5. From this, it was determined that there are cracks present on the surface before and after. However, post heat treatment and bending test, the width and densities of the crack increase. Further investigating the effect of these cracks on the resistance measurements, it was found that the existing defects may affect the growth behavior of the nanowires but they are not present at the level to change the conductivity.

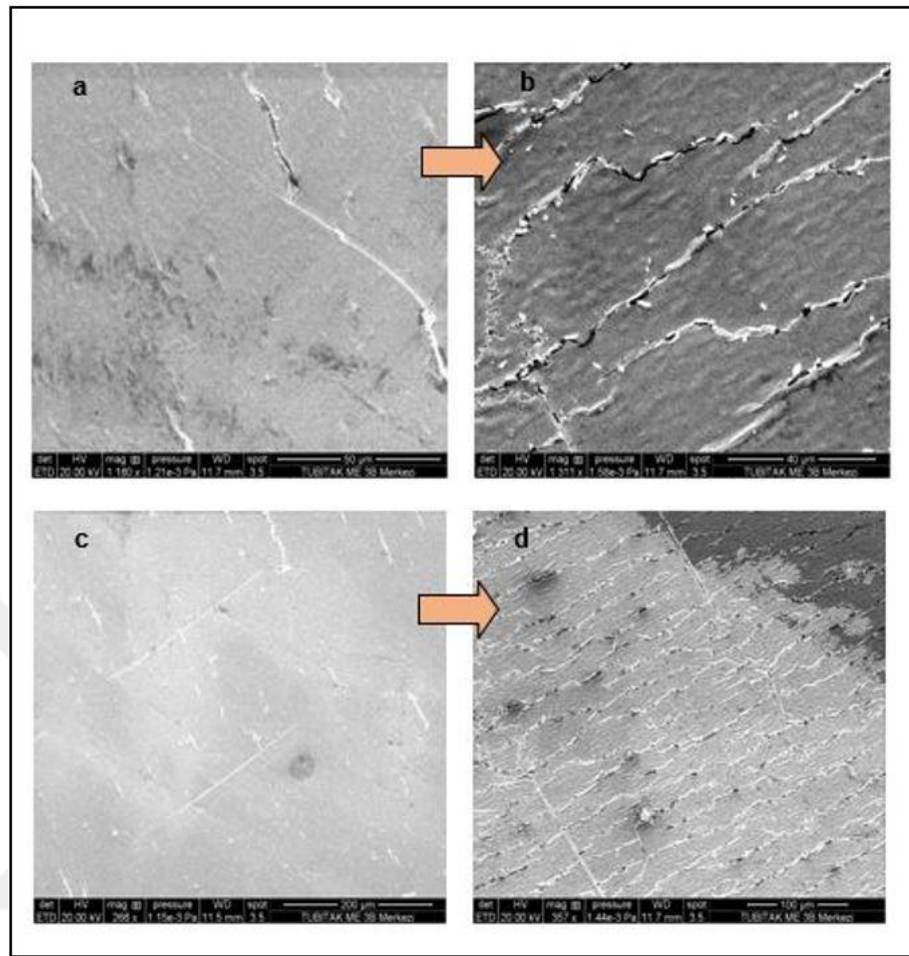


Figure 4.5 SEM images of ITO-PET (a) sample 1 before heat treatment, (b) sample 1 after heat treatment, (c) sample 2 before heat treatment, and (d) sample 2 after heat treatment.

4.2. SEEDING LAYERS

In this study, four different seeding layer counts were conducted: one layer, three layers, five layer and ten layers. As stated above, this layer is important because it promotes the growth of the zinc oxide nanowires. Briefly, the process of heating the growth solution leads to the zinc oxide seeds begin to come together to form larger diameters of the ZnO nanowires. The temperature is an important factor because studies have shown that at the temperature range (60 – 80 °C) lateral and axial growth are instigated and with the increase of temperature above this range, the growth type that is promoted more becomes axial growth only. This is of

importance since the temperature variable strongly affects the growth kinetics of the ZnO nanowires with regards to the c-axis [0001] direction(42). Alongside this, the thickness of the seed layer also effects the formation of the nanowires and their morphological and structural properties. For this reason, XRD analysis was conducted to analyze the different phases on the substrate and enough that there is seeding solution present, post annealing. Figure 4.6 below represents the XRD graph for the different seed layers, one, three and five. Using the ICDD Card No: 4-8-3506 to match the components present to zinc oxide to assure that the seeding layers are present on the substrates.



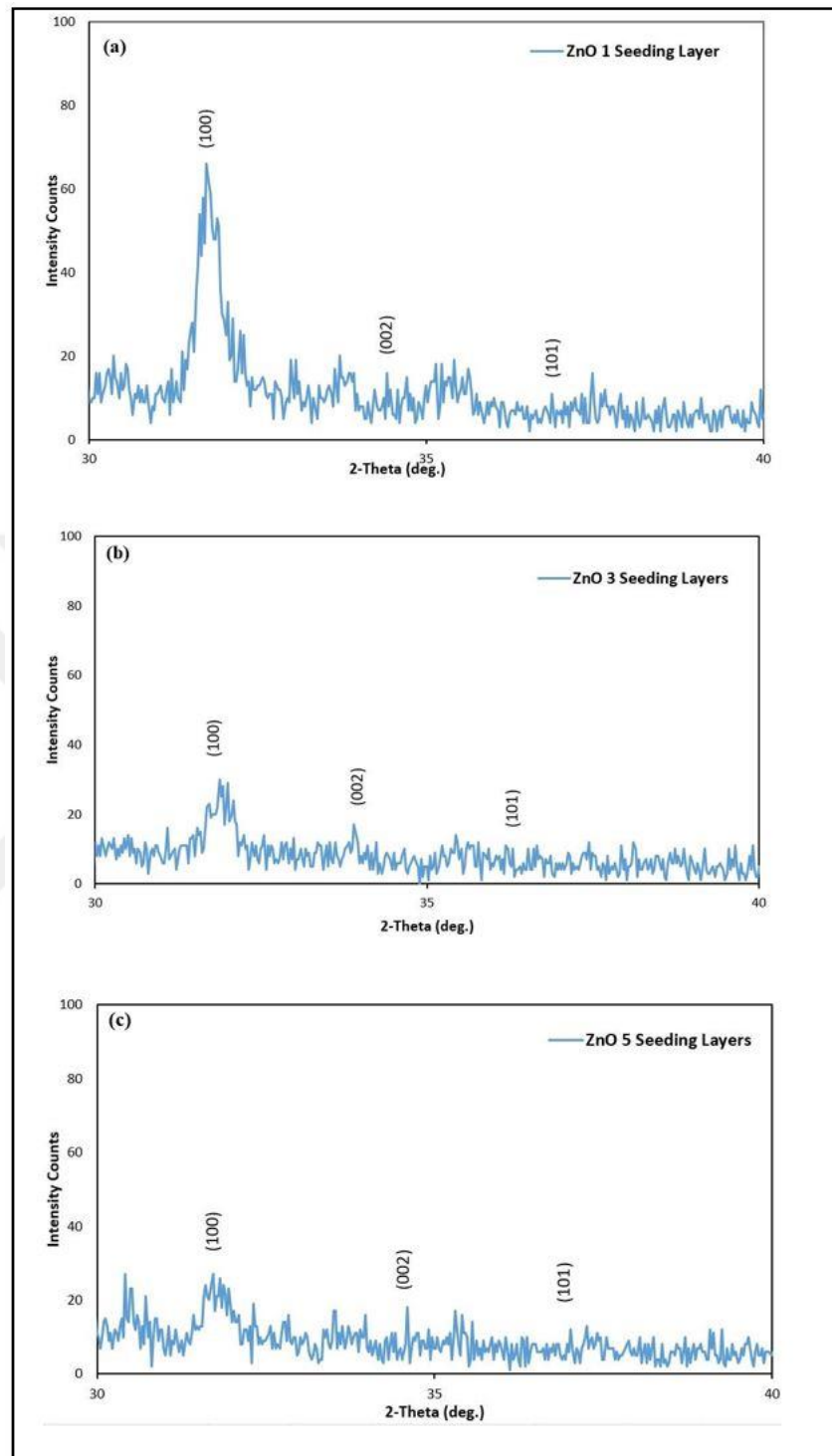


Figure 4.6 XRD image of ZnO (a) one, (b) three, and (c) five seeding layers using ICDD Card No: 4-8-3506 to identify the zinc oxide components.

4.3. ZNO GROWTH

Upon completion of the growth process, the substrates were analyzed using the x-ray diffraction method. This was to understand the preferential alignment of the nanowires after growth and to confirm that they exhibited a hexagonal shape at the cross-section. Card number 04-008-3506 describes a zinc oxide compound which indicated that the nanostructures on the surface have a hexagonal shape when grown at 90°C. According to the powder diffraction chart, the most severe diffractions of the ZnO compounds with hexagonal crystal system should be taken from the (101), (100), and (002) planes, respectively. (100), (002), (101), (102), (110), (103), and (200) of the hexagonal ZnO structure in all three samples grown in different layers and times on the ITO-GLASS substrates. This can be seen in the graphs presented below in Figure 4.7, 4.8, and 4.9. To confirm that they grow in a vertical direction, the intensities and 2θ angle values were noted. The d-spacing (002) projects a strong peak at 34° (2θ) which indicated that the nanowires are aligned in the c-axis direction, confirming that they are vertical.

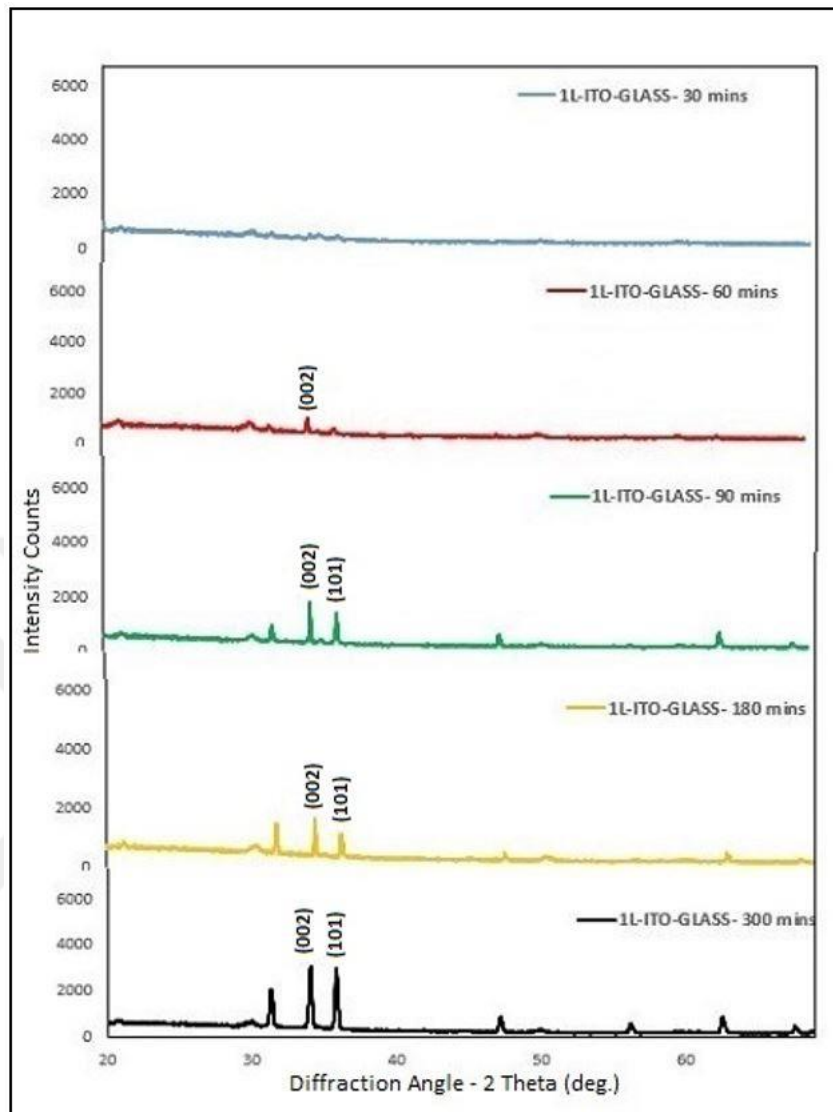


Figure 4.7 XRD results of ZnO hydrothermally grown nanowires with a variety of growth times for one seeding layer on ITO-GLASS.

The Figure 4.7 above presents the different growth times for one seeding layer following the same conditions of solution concentration and growth temperatures. It is clear that with the increase of growth time, the intensity of the peaks are higher. It is important to consider the ratio between (002) and (101) plane as it indicates the quantity of the ZnO nanowires that are vertically aligned. For one seeding layer, this ratio is considered to be very small meaning majority of the nanowires are not in the vertical direction.

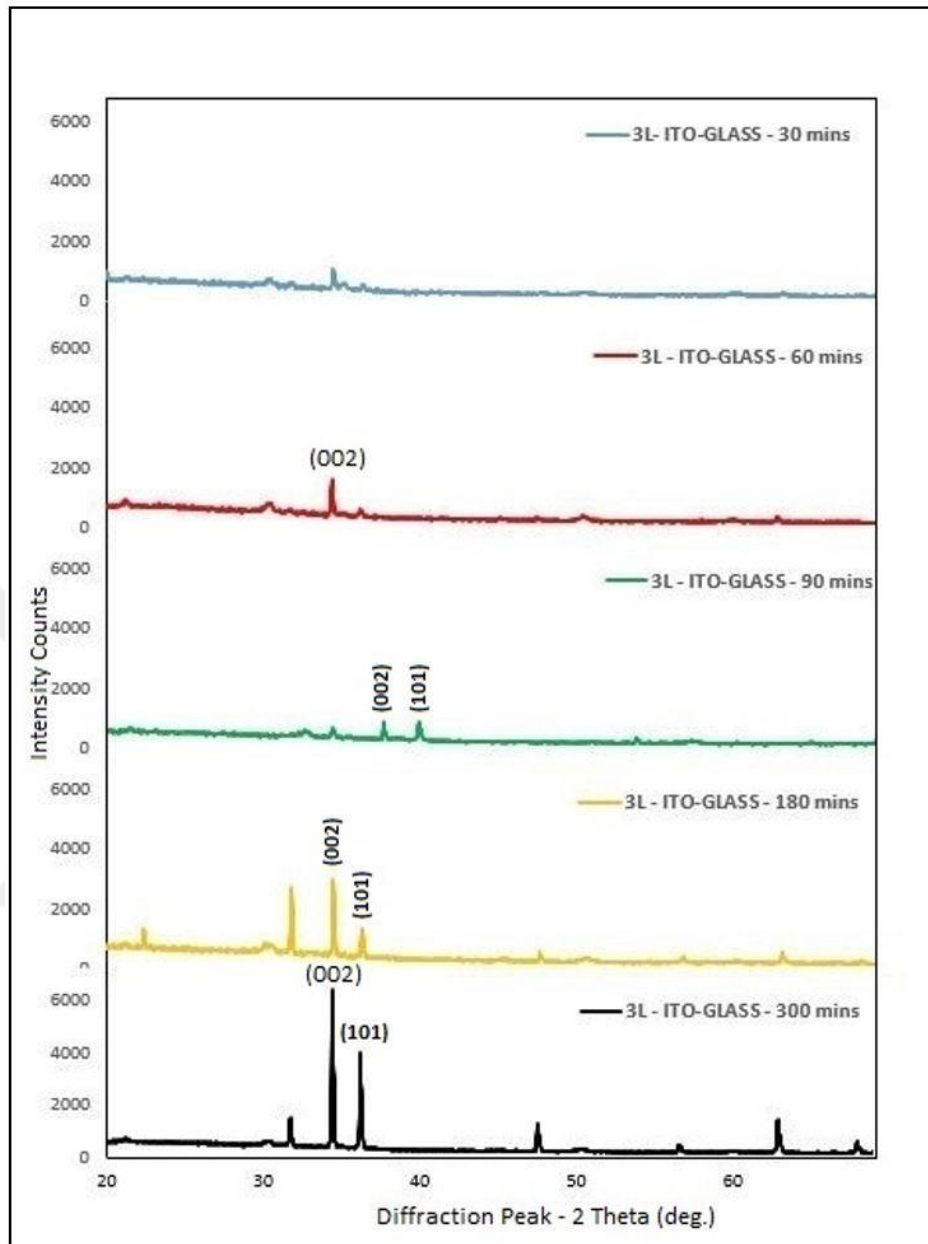


Figure 4.8 XRD results of ZnO hydrothermally grown nanowires with a variety of growth times for three seeding layers on ITO-GLASS.

From Figure 4.8 above, the effect of increasing the number of seed layers on the ITO-GLASS substrates is significant. The intensity counts for peaks (002) and (101) are higher when compared to one seeding layer. In addition to this, the ratio between the two planes is more than that of one seeding layer denoting that more nanowires are vertically aligned in the case of three seeding layers.

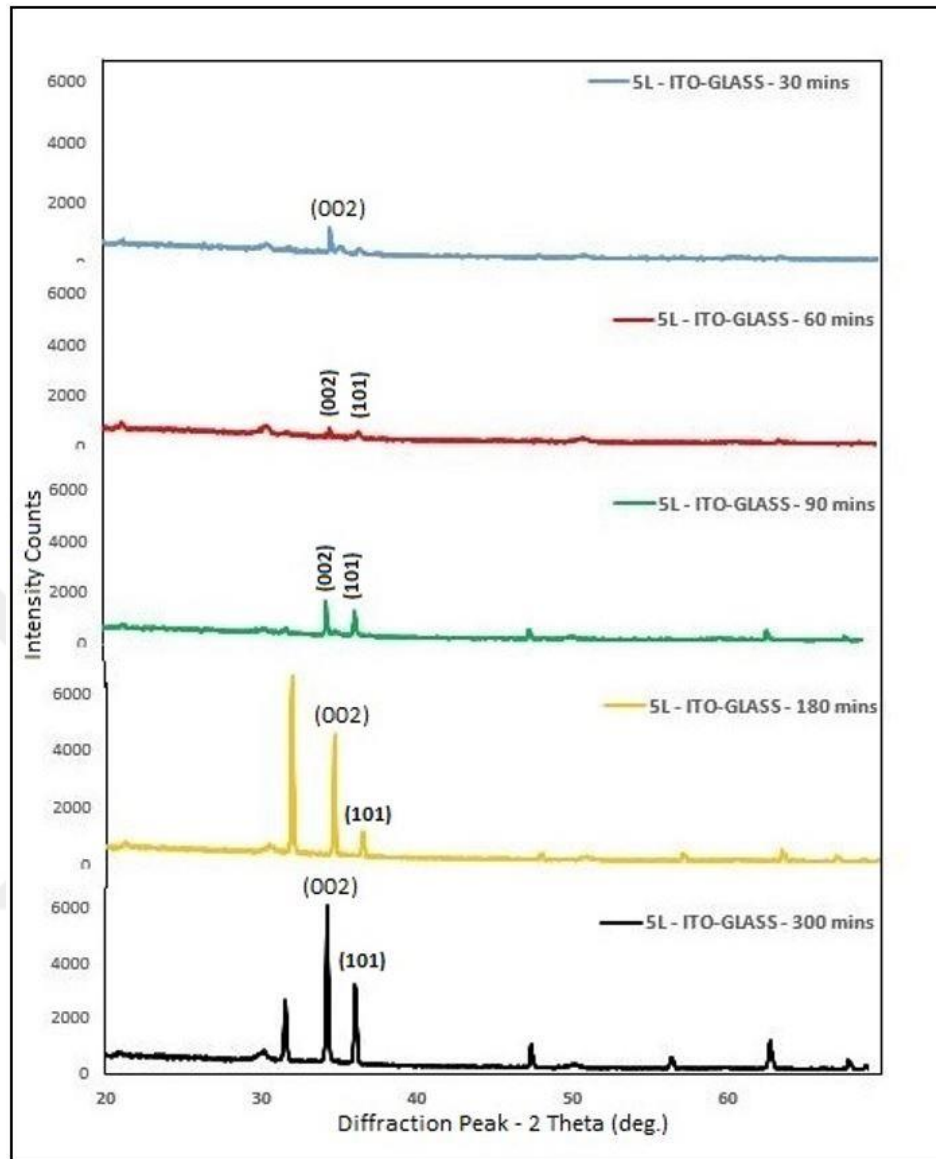


Figure 4.9 XRD results of ZnO hydrothermally grown nanowires with a variety of growth times for five seeding layers on ITO-GLASS.

In the case of five seeding layers, the peaks for both (002) and (101) are more intense than 1L and 3L seeding. With regards to the ratio, it is also larger than that of previous layers. This is clear in Figure 4.9 above.

Based on the results found from the different growth times and layers prepared, it can be seen that one layer of seeding shows less growth and nanowires vertically aligned than layers three and five layers. However, three seed layers show higher intensity counts at a diffraction

angle of 34.4° pointing out that more ZnO nanowires are present when ZnO nanowires were grown for 300 minutes. In the case of 180 minutes of growth, five layers showed better growth and alignment of the ZnO nanowires. From these studies, it can be concluded that 300 minutes of growth with five seeding layers results in the best quantity and quality of vertically aligned ZnO nanowires. Comparing the quality and quantity of the nanowire growth in terms of time, it is clear that the longer the duration of the growth, the more nanowires present. This is compatible with the literature found (43). This is clearly seen when comparing each ZnO seed layers to growth time. The pattern in the increase of the intensity peak is clear as the duration increases.

To further analyze the experimental conditions for hydrothermal growth of zinc oxide nanowires, a set of experiments were conducted. Following the procedure described above, four different samples were prepared: five and ten layers of ZnO seeding on ITO coated glass substrate and five and ten layers of ZnO seeding on ITO coated PET substrates. The number of layers was chosen based on the results presented above and to further study whether there is a threshold of number of seed layers that restricts the growth of the nanowires. Based on the XRD analysis of the glass substrate, it was found that with the addition of more seed layers, the intensity of the growth increased. The preliminary tests were conducted by using the ITO coated glass substrates because they are more practical to work with and more accessible, then the finalized conclusions were tested on PET substrates to evaluate if the conditions were the same for both of the substrates. Since it was found that the longer the growth duration was set, the better the quality and quantity of nanowires were produced. As well as the addition of more ZnO seed layers showed better results, meaning that five layers produced better results than three layers (44). For this reason, it was decided to try five and 10 layers of seeding solution grown for 300 minutes on both glass and PET substrates. The XRD pattern for the glass substrates is shown below in Figure 4.10. It can be seen that for ten seeding layers, the intensity level of the (002) plane is much higher than that of five layers. This means that the quantity of nanowires produced is much more than that of 1L, 3L, or 5L. It is also important to compare the ratio of intensity counts for (002) to (101) because it indicates the directionality of the nanowires. Base on the graphs, it is clear that for 10L seeding, the ratio is larger than the other seeding layers. This indicates that there should be a higher percentage of vertically aligned nanowires present on the 10L seeding ITO-GLASS substrate. According to card number 04-008-3506, this 2θ value

projects (002) d-spacing which, as previously stated, points out that the ZnO nanowires grown are vertically aligned in the c-axis direction. From these results, it can be seen that the quality and quantity of the growth are heavily dependent on the seed layers present (45). The growth time also relied on the previous results which indicated that the longer the duration the more nanowires were present.

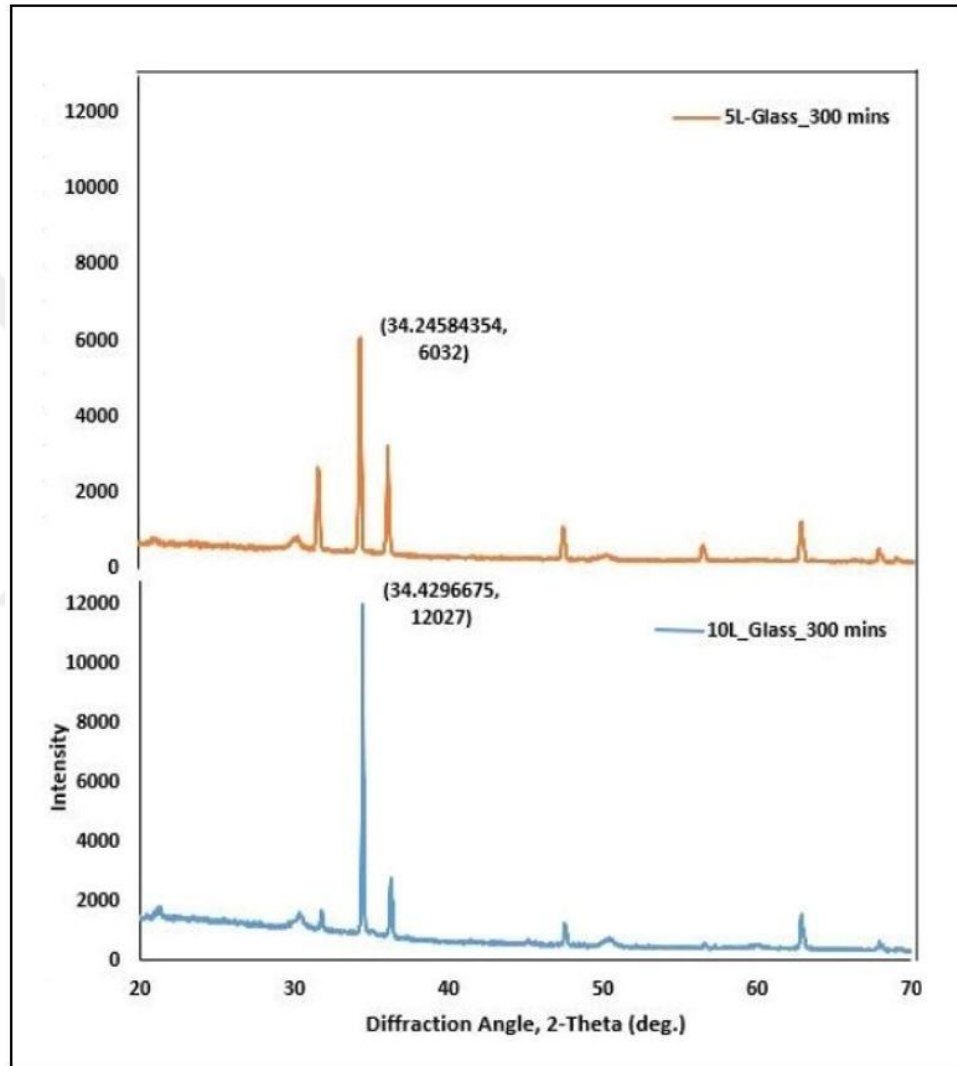


Figure 4.10 XRD analysis of zinc oxide nanowires hydrothermally grown on ITO coated glass substrates using both five and 10 layers of seeding for a duration of 300 minutes.

When using ITO-coated PET substrates for assisting the growth of the nanowires, the results showed otherwise. As seen below in Figure 4.11, in the case of PET five layers of seeding produced better results and higher intensity peak levels than the 10 layers of seeding. This may be the case since increasing the seed layers increases the concentration of the pores for

the nanowires to grow which results in overcrowding on the substrate leading to restriction of the growth. The ratio between (002) and (101) is less than that of ITO-GLASS, which should indicate presence of ZnO nanowires are non-vertical directions.



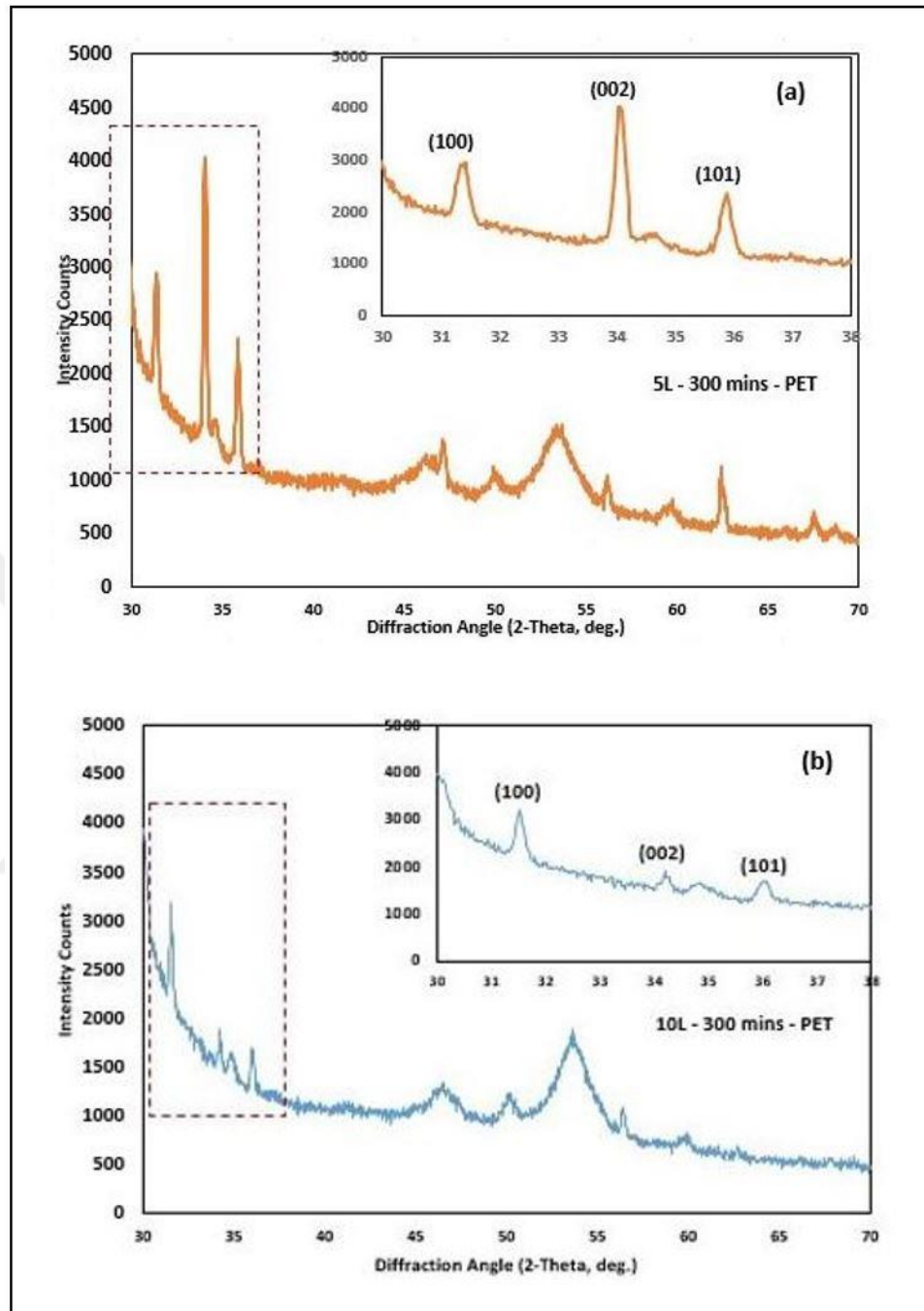


Figure 4.11 XRD analysis of both (a) 5L and (b) 10L seed layers for hydrothermally grown ZnO nanowires on ITO coated PET substrates.

Based on the XRD results found, it can be said that longer growth durations lead to better production and crystallization of zinc oxide nanowires, assuming the concentration of the growth solution is sufficient and the temperature is kept at 90°C. This process can be linked to what is known as the crystallization theory. This theory is centered on the idea that at a specific condition (set temperature, pressure, etc), the crystallization process of a compound is determined by its limited solubility in a solvent. The crystal lattice of the crystalline material is found to have high regular internal structures due to their formation process.

To further prove the morphology of the nanostructures hydrothermally grown, scanning electron microscopy (SEM) was studied, both cross-section and surface views. This technique uses high magnifications to be able to devise images with both high resolution and magnification and can produce such images by using an electron beam. By conducting this type of analysis, researchers can generate two-dimensional images that provide specific information about the samples such as the chemical composition or the external texture. With the EDS (Energy Dispersive X-ray Spectroscopy) component, the elements found on and in the sample can be examined. The samples chosen for SEM analysis were based on the XRD results produced. Some SEM images were taken for two different growth durations: 180 minutes and 300 minutes. For 180 minutes of growth on glass substrates, 1L (a & b) and 3L (c & d) cross-sectional views are presented below in Figure 4.12. It can be seen that the majority of the nanowires are in the vertical direction and exhibit an average length of 2.113 μm for 1L seeding. In the case of 3L seeding, the ZnO nanowires were found to have longer lengths with an average value of 2.956 μm . Based on this data, it is expected that the 5L and 10L seed layers produce longer nanowires than 1L and 3L when grown on glass.

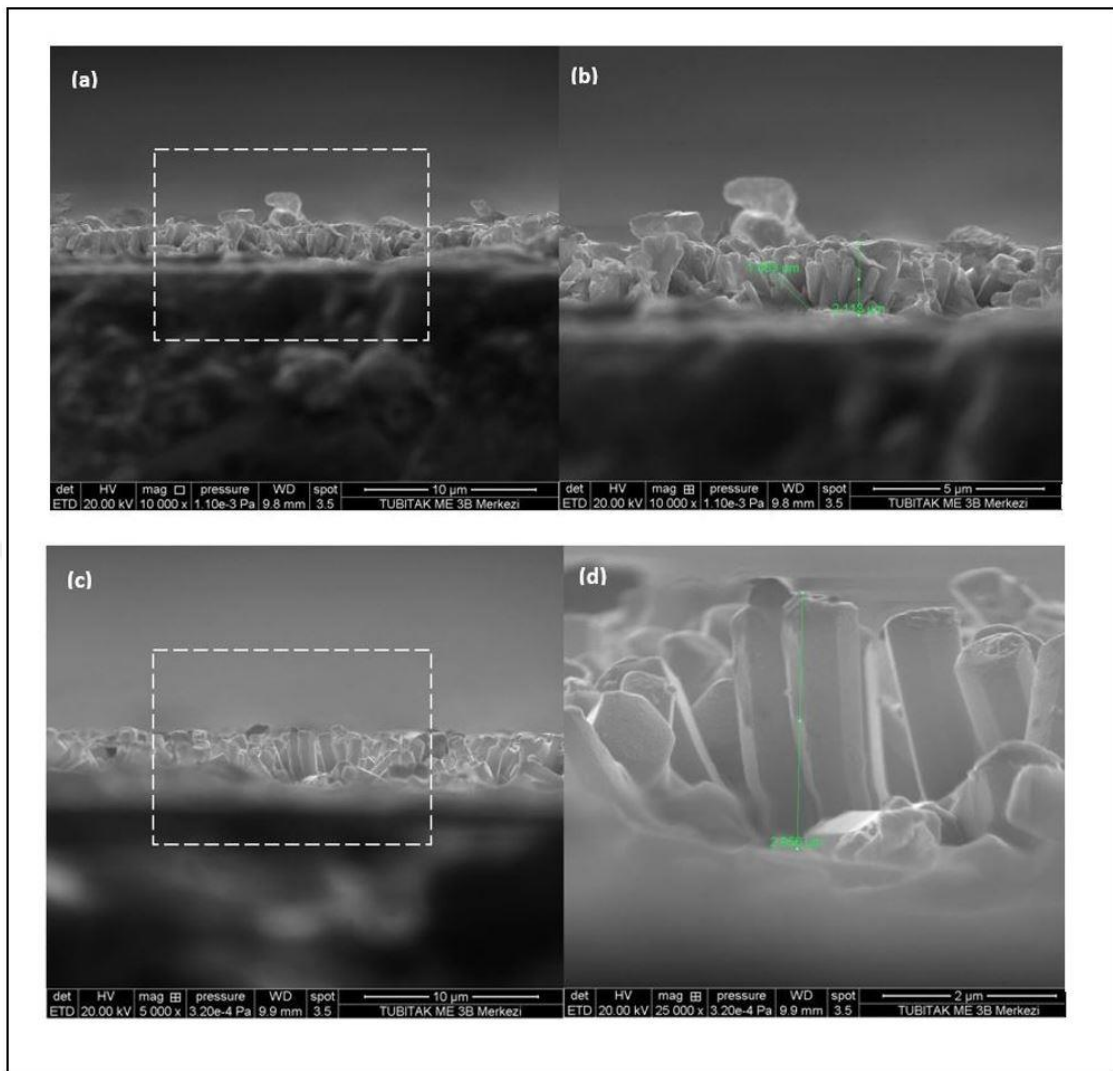


Figure 4.12 Cross-sectional SEM images for (a & b) 1L and (c & d) 3L seed layers for ZnO nanowires grown on ITO coated glass substrates for 180 minutes.

When comparing the ZnO nanowire growth between ITO-GLASS and ITO-PET substrates using five seed layers and 10 seed layers for 300 minutes, according to the XRD data, it was found that the growth was better when using five seeding layers on ITO-PET substrate. On the other hand, 10 seeding layers on ITO-GLASS showed higher intensity peaks meaning that the growth of the ZnO nanowires was with better quality and quantity. To further study this, SEM analysis for the four samples (5L & 10L ITO-GLASS and ITO-PET) was conducted and is presented in Figure 4.13 and Figure 4.14 below. According to this analysis, it was found that five seeding layers on ITO-PET substrate produced better quality and quantity of hydrothermally grown ZnO nanowires. Random nanowires were chosen to

measure their lengths and diameters. It was found that 5L ITO-PET produced longer nanowires (3.426 μm , 2.909 μm , and 2.862 μm) with wider diameters (601.3 nm, 613.2 nm, 876.6 nm) than 10L ITO-PET. This further confirms what the XRD results conveyed that growth on PET substrates produced more desirable growth when five seeding layers was used. In terms of ten seed layers on PET substrates, the length of the randomly selected nanowires was 1.122 μm , 1.440 μm , and 1.399 μm with diameters of 376.7 nm, 306.0 nm, and 405.0 nm. When compared to glass substrates, 10 seeding layers produced length of 1.090 μm and 1.313 μm from randomly selected nanowires. The hexagonal shape of that the nanowires are expected to portray is also clearly seen in all substrates regardless of seeding layers or substrate type used. Confirming the XRD results above, the effect of the ratio of (002) to (101) is seen. Ten seeding layers on ITO-GLASS had the largest ratio and based on the SEM images (e & f) it is clear that the majority of the nanowires are vertically aligned. However, the SEM images for ITO-PET shows most of the nanowires in multiple directions due to the ratio being lower.

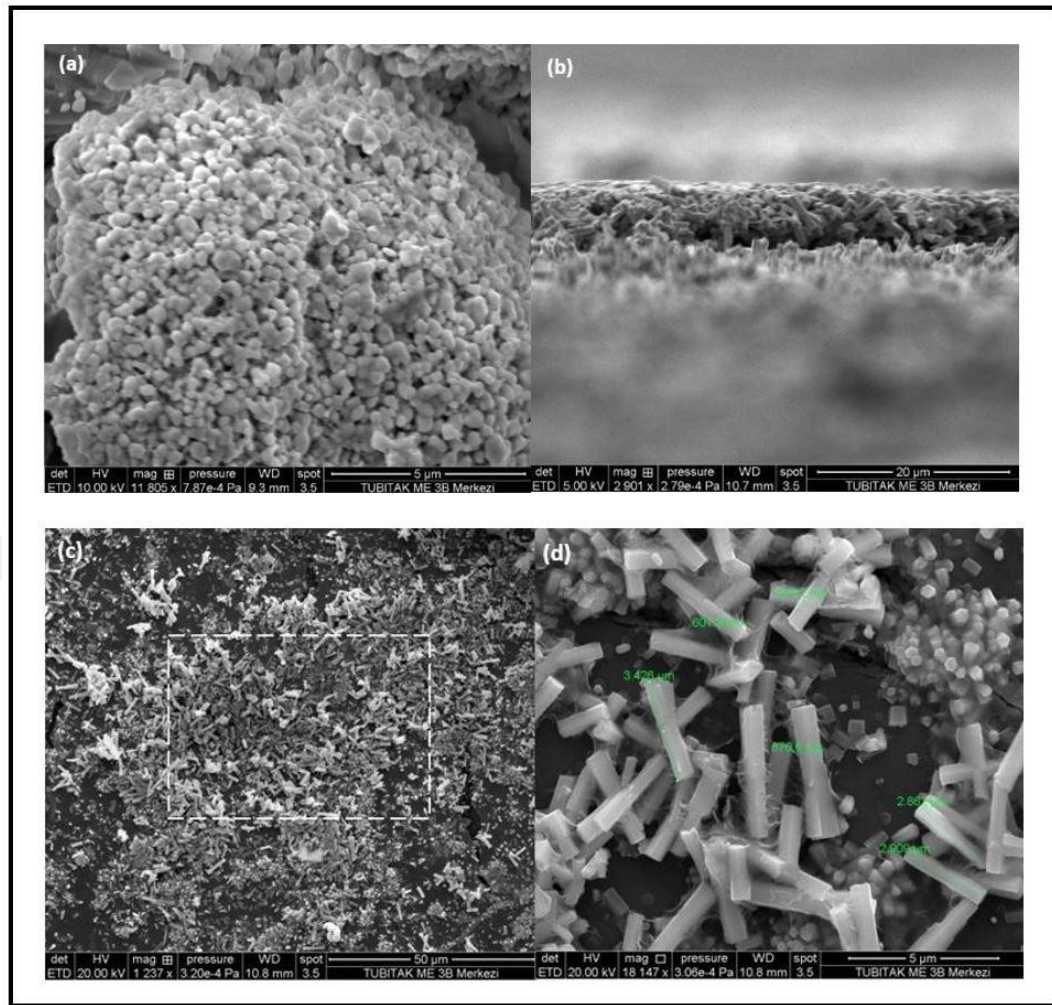


Figure 4.13 SEM images for substrates (a) 5L-ITO-GLASS (surface), (b) 5L ITO-PET (cross-section), (c & d) 5L ITO-PET (surface).

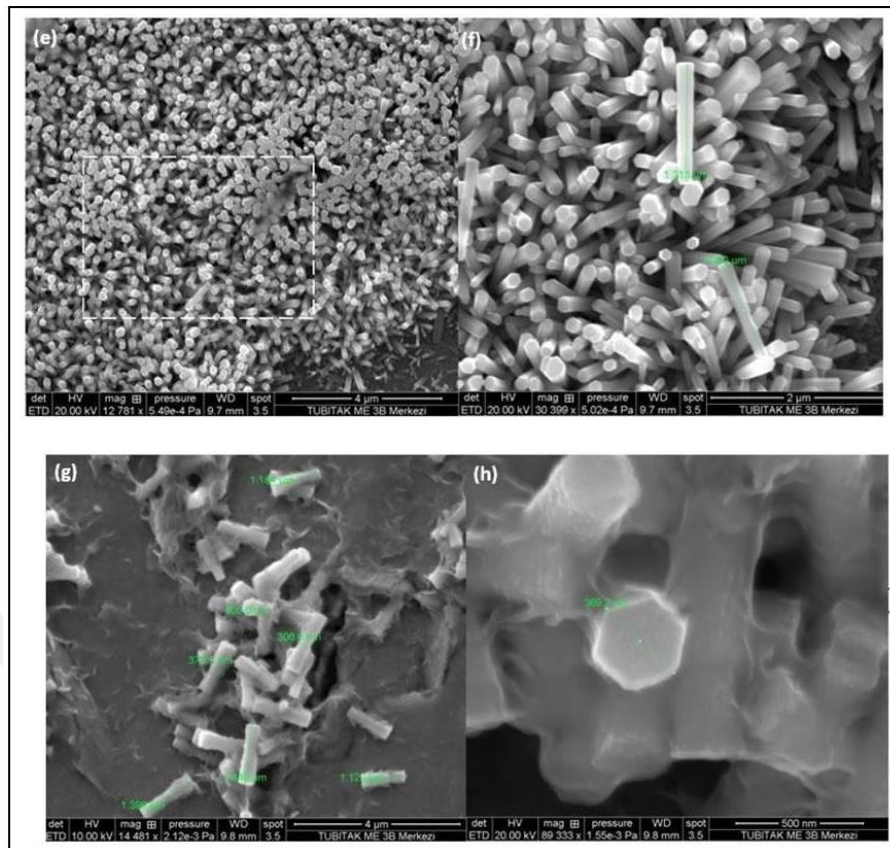


Figure 4.14 SEM images for substrates (e & f) 10L ITO-GLASS (surface), and (g & h) 10L ITO-PET (surface) all grown for 300 minutes.

Ultraviolet-visible spectroscopy (UV-VIS) is classified as a quantitative technique that analyzes the extent of a chemical substance to absorb light. It is very important to have a reference sample since it will be used as a guide for understanding the different light intensities absorbed by the samples. The two different measurements that take place are absorption and transmission measurements which allow for the determination of the concentration of the substance, which is done by examining the detector and counting the number of photons that reach it (46). The transmission for the samples was measured and the transmission percentage was calculated. The results can be seen in Figure 4.16 and Figure 4.17 below, representing each transmission percentage for visible light, IR light, solar light, and UV light.

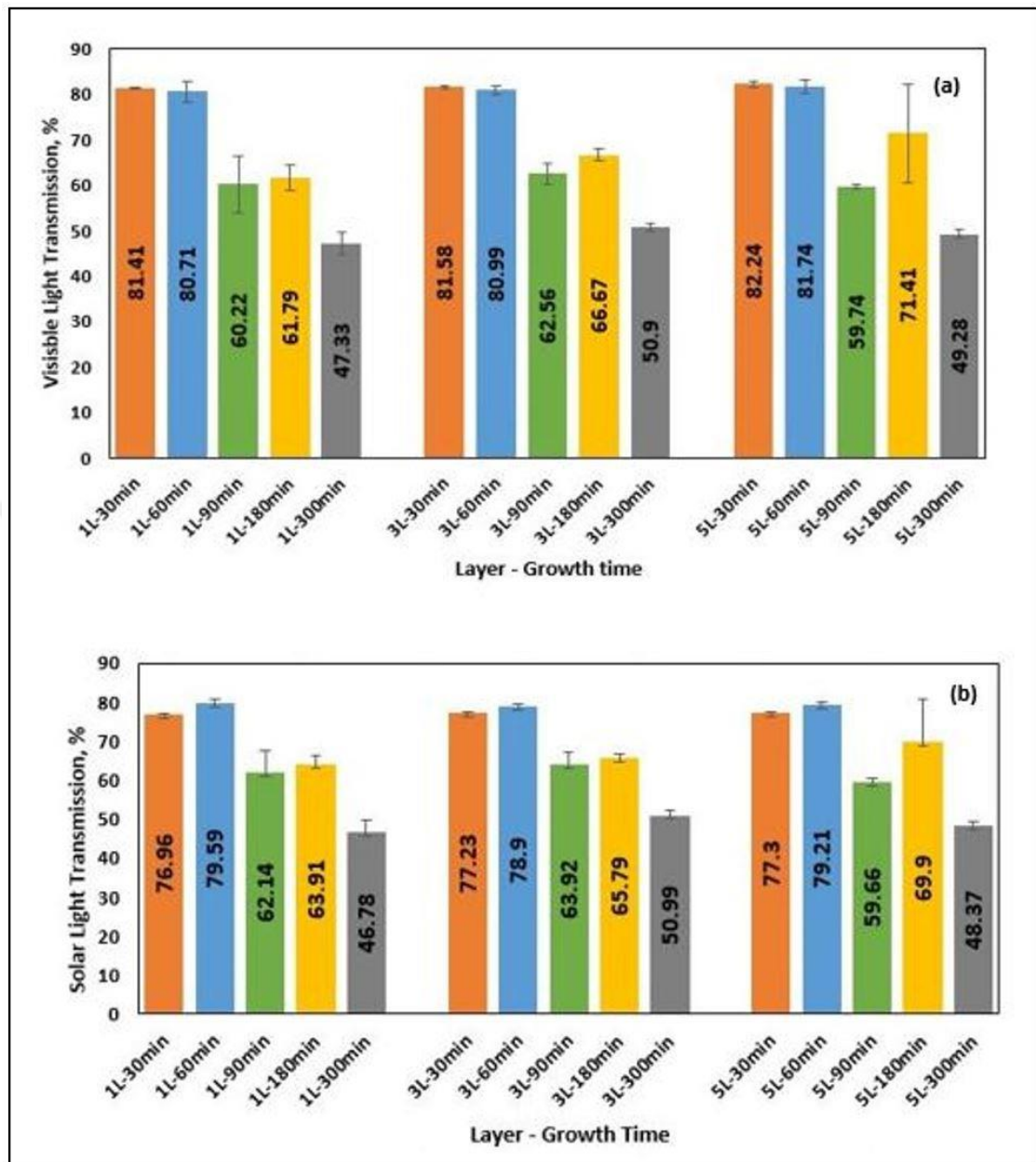


Figure 4.15 UV-VIS spectroscopy results with regards to (a) visible light and (b) solar light.

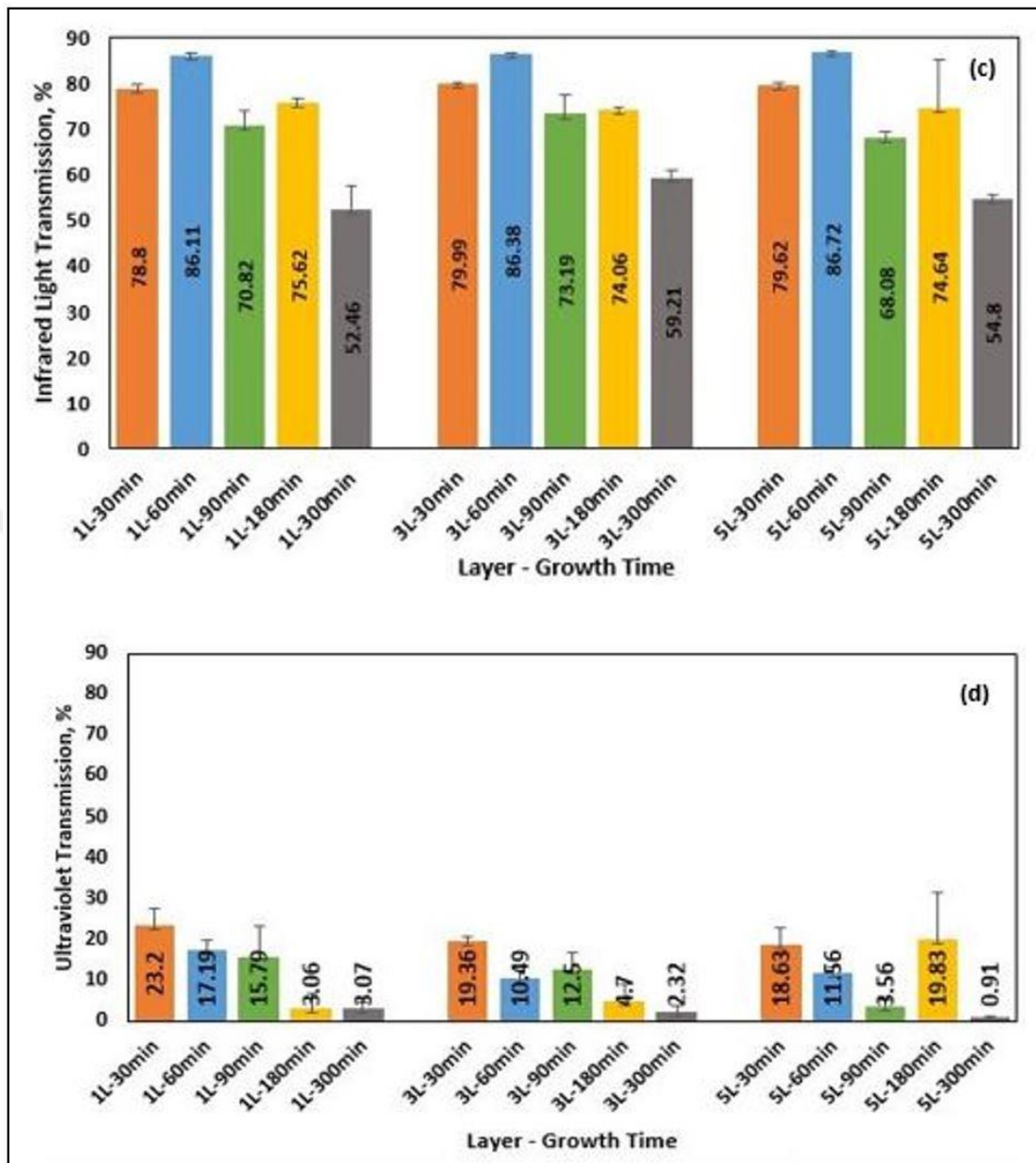


Figure 4.16 UV-VIS spectroscopy results with regards to (c) Infrared light, and (d) ultraviolet light.

Based on the figures above, it can be seen that the more components on the surface, the less the transmission percentage is. The conclusion that can be made from this is the increase in seed layers leads to more constituents and nanowire growth present leading to a decrease in transmission percentage. It can also be seen that with the increase in growth time, the transmission percentage decreases as well. For instance, take a closer look at 90 minutes of growth for all layers (one, three, and five layers). For one layer of seeding, the transmission

percentage was found to be around 15.79 percent, while for three layers it was less, around 12.50 percent. For five seeding layers, the transmission percentage drastically decreased to 3.56 percent.

AFM is an important technique to consider since it allows for the assessment of some physical features of the substrates such as surface roughness of the surface. This is important because ZnO nanowires have many applications dependent on piezoelectric and electromechanical behaviors and these properties require constant external forces(47). The average of eight analyses of surface roughness values was measured for all of the different samples prepared and the results are presented in Figure 4.18 below.

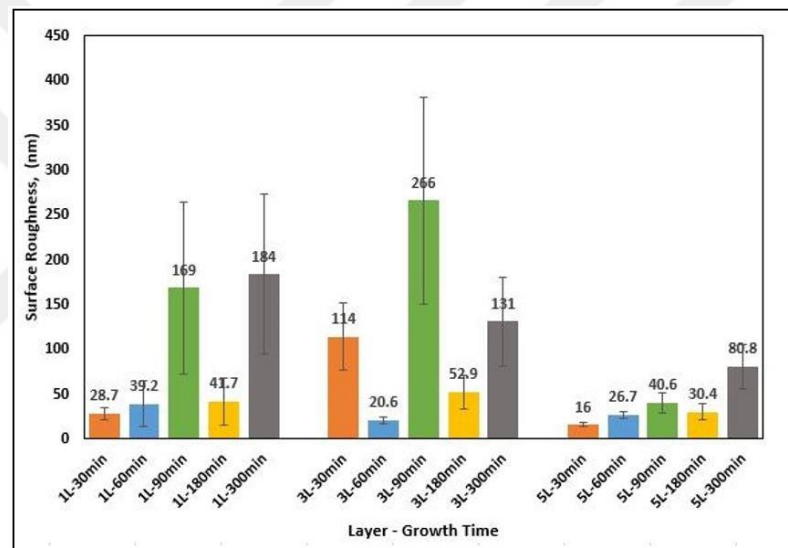


Figure 4.17 Average surface roughness for all layers and growth times conducted.

Apart from the surface roughness values, surface topography images were taken for each sample to examine the surface and constituents of the surface. This is important because it allows for understanding the shapes of particles on the surface. The three-dimensional surface topography of the samples are presented below in Figure 4.19 and Figure 4.20.

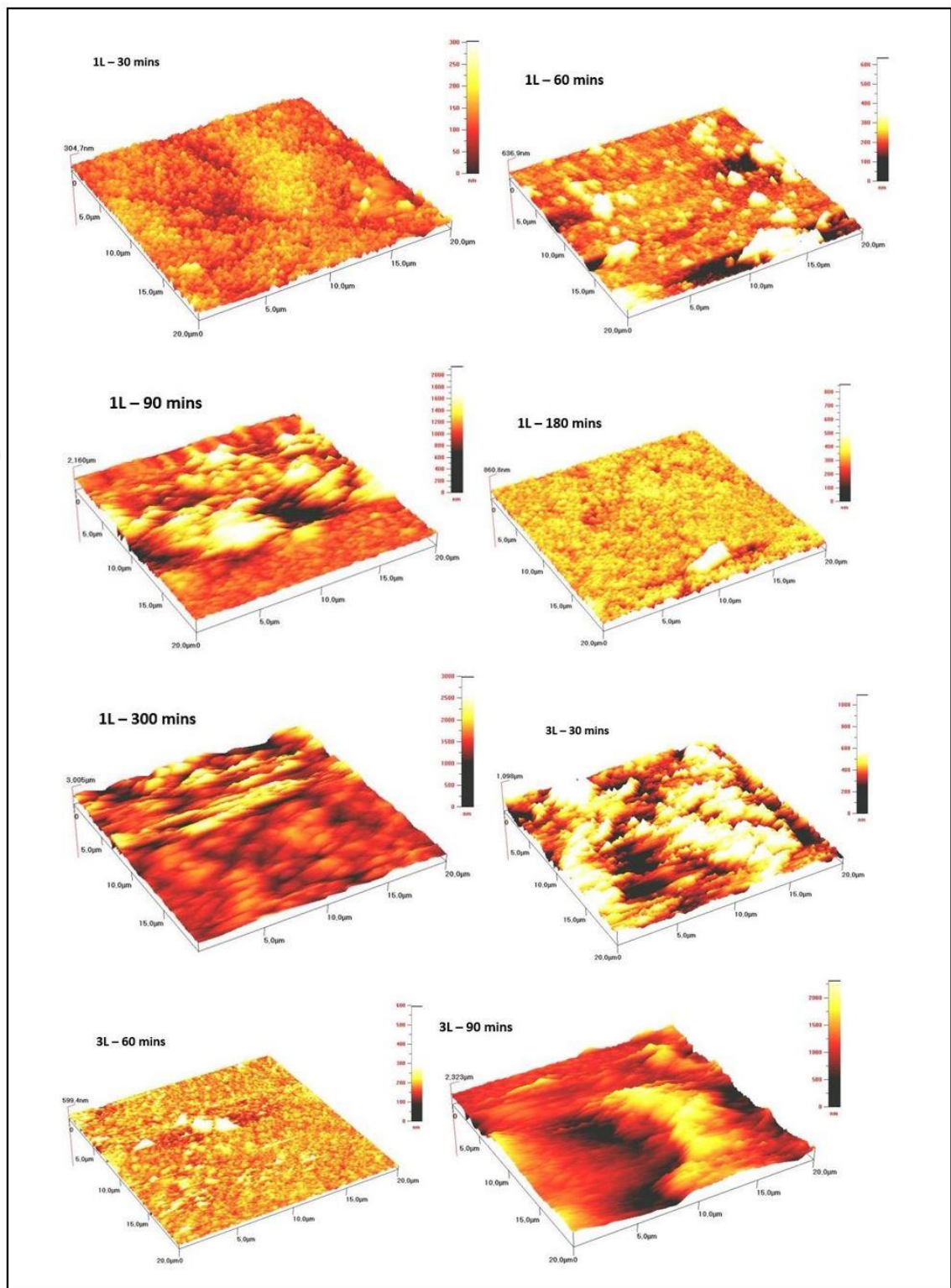


Figure 4.18 AFM analysis 3D images for all glass samples.

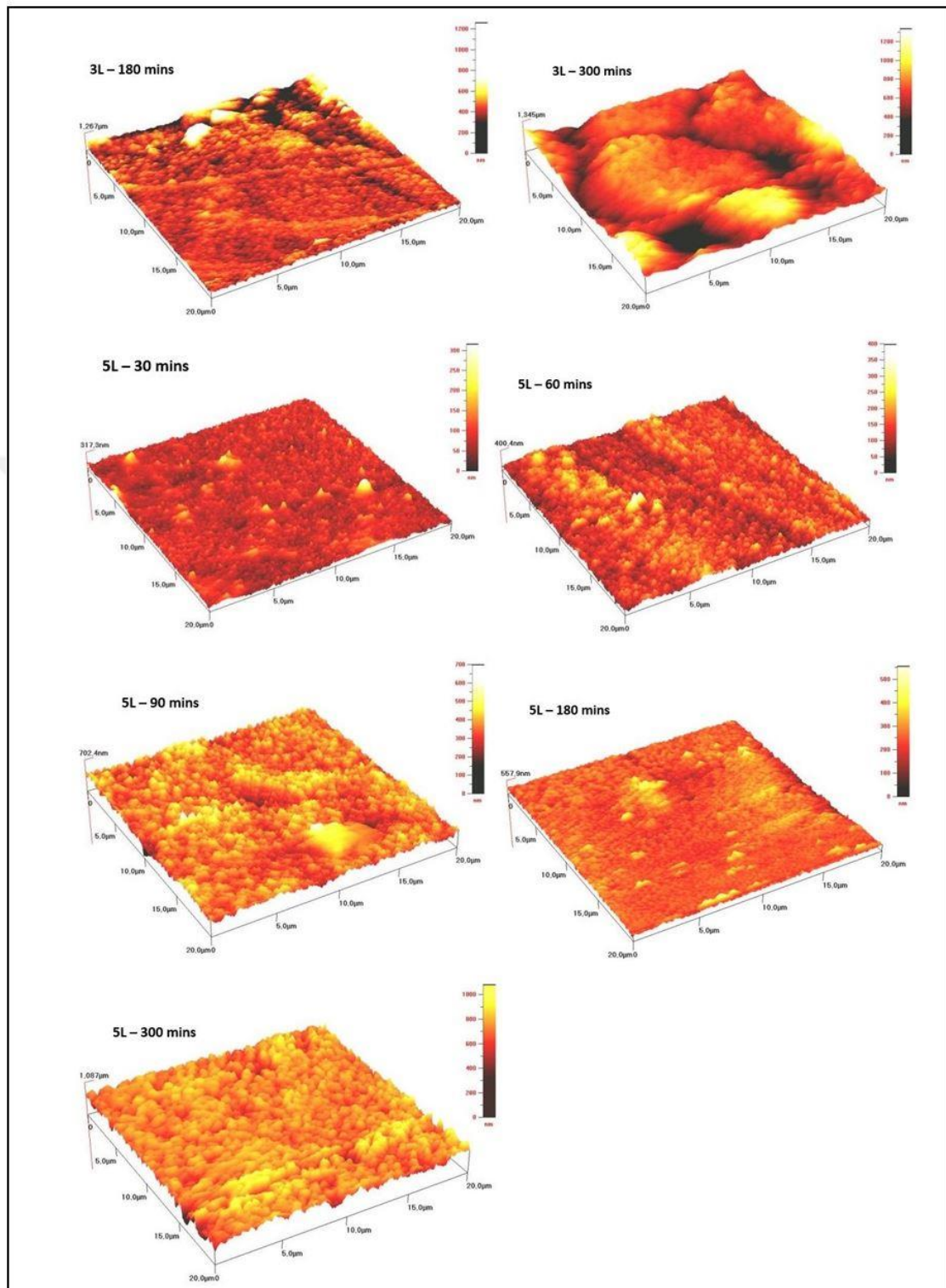


Figure 4.19 AFM analysis 3D images for all glass samples.

4.3. CONDUCTIVITY

In order to determine the energy potentials of ZnO nanowire arrays synthesized, certain analysis was conducted using AFM device with the semiconductor parameter analyzer to measure the voltage/current characteristics. In order to control the semiconductor parameter measurement system with AFM, three different studies were carried out. Firstly, voltage values were measured without operating the AFM device. This is required in order to remove the signals originating from the noise. Following this, engage mode was set meaning that the Pt probe moves downwards and measures the voltage and current operating in AFM non-contact mode. Finally, the measurements were conducted on each sample five different times.

5. CONCLUSION AND FUTURE WORKS

This section concludes the results of the thesis and the potential future works that can come as the different results found.

5.1. CONCLUSION

In this thesis, the synthesis of zinc oxide nanowires on both ITO coated glass and PET substrates using hydrothermal growth method was investigated. The hydrothermal method was explained along with characterization methods for ZnO nanowires. Simply, the hydrothermal method has many advantages over the other synthesis techniques and is generally preferred due to its simplicity and low processing costs, specifically due the working temperatures being low. Typically, this method requires the presence of zinc acetate combined with HMTA in solution where this solution is set to a certain temperature. The operating temperature is important because it effects the growth of the nanowires and is known to be low in hydrothermal growth synthesis method. With the use of this method, the growth of zinc oxide nanowires was possible.

After the growth of the nanowires, a variety of characterization techniques was report out to evaluate the quality of the growth. The different number of seeding layers (1L, 3L, 5L and 10L) as well as the growth durations varied to examine the characteristics and properties of the nanowires produced while using two different substrates, ITO-GLASS and ITO-PET.

The directionality of these nanowires is yet to be improved however based on the different studies conducted, it can be concluded that in the case of ITO-GLASS substrates, the more seeding layers coated on the surface with longer growth durations produces more aligned ZnO nanowires in c-axis direction. With regards to ITO-PET, the studies conducted so far indicate that increasing seeding layers may not be the ideal solution for producing these nanowires. Since it is aimed to hydrothermally grow the ZnO nanowires as parallel to the c-axis as possible, it is important that the orientation occurs in the (002) plane. The direction is important because it allows for these nanowires to be integrated into multiple devices such as nanogenerators. Based on the different studies conducted, ten seeding layers on ITO-GLASS presented the most vertically aligned nanowires, confirmed with SEM and XRD analysis. Transmission and absorbance properties of the ITO-GLASS substrates were also

measured to analyze the impact of longer growth times. Since more substituents are present on the surface with longer growth durations, these levels of absorbance decreased according to UV-VIS characterization technique.

5.2. FUTURE WORK

In this thesis, the different conditions for hydrothermally growing zinc oxide nanowires were investigated. These conditions included concentrations of seeding solution and growth solution, number of seeding layers, annealing heat treatment temperatures and duration, growth solution temperature, growth duration, and substrate type (ITO-GLASS and ITO-PET)., In terms of ITO-GLASS substrates, coating more seed layers (20 layers, 30 layers...etc.) can be done to further investigate the quantity of the vertically aligned nanowires as was as quality. The duration of the annealing heat treatments can be further studied to improve the structural properties of the ZnO nanowires. Longer growth durations can be carried out considering sufficient concentration of the growth solution is present to find out the extent of the lengths that the nanowires can be grown while still retaining their properties and characteristics. The electrical measurements (voltage and current) measured using AFM device with the semiconductor parameter analyzer can be further studied to explore the electrical potential of the ZnO nanowires grown.

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