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Bachelor's Thesis

Hydrothermal Synthesis of ZnO Nanorods

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Abstrakt:

Bakalárska práca sa zaoberá rastom nanorodov oxidu zinočnatého pomocou hydrotermálnej syntézy, pričom sa zameriava na optimalizáciu parametrov syntézy a získanie poznatkov o základných mechanizmoch rastu. ZnO nanorody, známe svojimi charakteristickými optickými a elektronickými vlastnosťami, nachádzajú široké uplatnenie v oblastiach, ako sú optoelektronika a nanotechnológie. Hydrotermálna metóda sa vyznačuje miernymi reakčnými podmienkami a vysokou účinnosťou.

V rámci tejto bakalárskej práce boli skúmané vplyvy rôznych parametrov syntézy vrátane teploty, substrátu a reakčného času na rast nanorodov. Charakterizácia štruktúrnych a morfológických vlastností syntetizovaných nanorodov bola skúmaná pomocou skenovacieho elektrónového mikroskopu. Výsledky ukazujú, ako rôzne parametre ovplyvňujú usporiadanie a kryštalinitu nanorodov, čo poskytuje poznatky o optimalizácii procesu syntézy pre požadované nanoštruktúry.

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Abstract:

This bachelor's thesis investigates the hydrothermal synthesis of zinc oxide nanorods. It is examined with an emphasis on the optimisation of the synthesis process and the analysis of growth kinetics. Zinc oxide nanorods which possess unique optical and electronic characteristics are employed widely in areas such as optoelectronics, and nanotechnology. Given the mild reaction conditions and high efficiency, the hydrothermal process was employed for the synthesis of ZnO nanorods with a predefined shape and diameter.

Furthermore, the impact of temperature, substrate and reaction time on the synthesis of the nanorods has been thoroughly examined. The structural and morphological properties of the synthesised nanorods were determined by techniques including scanning electron microscopy. These results also establish how various parameters affect the alignment and crystallinity of the nanorods as well as the enhancement of the synthesis to yield specific nanorods.

Declaration

I declare that I have prepared the submitted work independently under the supervision of Mgr. Radim Čtvrtlík, Ph.D. and that I have used the resources cited and listed in the used bibliography.

Signed in Olomouc on:

Author's signature:

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1. Introduction

A lot of attention has been recently paid to studies on metal and semiconductor nanostructures because of their many intriguing physical and chemical characteristics and their many potential uses in nanotechnology [1]. They promise to possess innovative features and serve as an alternative to devices composed of thin layers of standard semiconducting materials.

Due to its unique optical, electrical, and piezoelectric capabilities, zinc oxide (ZnO), which has a band gap of 3.37 eV and a high exciton binding energy of 60 meV at room temperature, is a significant technological semiconductor [2]. The application of ZnO nanorods and nanowires in ultraviolet (UV) lasers [3], field emission devices [4], sensors [5], transistors [6], solar cells [7], piezo-nanogenerators [8], and light emitting diodes [9] has been the focus of significant research in recent years [10].

ZnO nanowires have been created using a variety of techniques like electrochemical method, vapour deposition, hydrothermal synthesis, or the sol-gel process. ZnO nanotube array production now relies primarily either on chemical vapour deposition or an electrochemical method [2]. In contrast to the other methods, hydrothermal synthesis is a reliable and affordable process for the creation of ZnO nanowires and can be carried out with basic equipment [10].

Our outcomes offer a solution for synthesising zinc oxide nanorods utilising just zinc acetate as the zinc source. The structure and size of the ZnO nanorods were examined by using a scanning electron microscope SEM.

2. Zinc Oxide

Zinc oxide (ZnO) is acknowledged as a material that exhibits a diverse range of applications due to its distinctive properties. The material is utilised in a number of high-tech fields, including piezoelectric transducers, optical waveguides, surface acoustic wave devices, varistors, phosphors, transparent conductive oxides, chemical and gas sensors, spin-functional devices, and UV light emitters. The most significant applications have been in spintronics and sensing technology, which demonstrate the versatility of the material [11].

2.1 Mechanical and Chemical Properties

Zinc oxide is notable for its distinctive properties such as enhanced chemical stability, a measurable electrochemical coupling coefficient, a wide range of radiation absorption and exceptionally high photocorrosion resistance. These qualities render it a versatile material [12]. In the materials science, zinc oxide is classified as a Group II-VI semiconductors and its covalence is in between the ionic and covalent semiconductors. It has a large energy band of 3.37 eV, a strong bond energy of 60 MeV, and good thermal and mechanical stability at the ambient temperatures, rendering it an ideal material for use in electronics, optoelectronics, and laser technologies [13]. Furthermore, due to its piezoelectric and pyroelectric properties, ZnO finds application in sensors, converters, energy generators, and photocatalyst for hydrogen production [14]. Due to its high hardness, rigidity and a rather high piezoelectric constant, the use of zinc oxide is of great significance in the field of ceramics. Furthermore, it exhibits low toxicity, high biocompatibility and biodegradability, which render it an appropriate material for use in biomedical and biodegradable systems [15].

2.2 Diverse Applications

1. Spintronics and Sensing

In the field of spintronics, ZnO is one of the most extensively researched materials, particularly when doped with the transition metals. Doping is the process by which the magnetic properties of ZnO can be enhanced, thereby rendering it suitable for use in the fabrication of spintronic devices that are vital for future generations of electronics [13].

Furthermore, the selectivity of ZnO for a number of gases, including ethanol, acetylene and carbon monoxide, renders it suitable for sensing applications. Furthermore, it is biocompatible and thus suitable for use in the biological field, including the construction of medical devices and sensors. It is also noteworthy that ZnO is an eco-friendly and chemically stable material, which is currently a focus of research in the development of environmentally friendly technologies [16].

2. Luminescence

The optical performance of ZnO, in particular its luminescence, has been the subject of considerable recent interest. Recent developments in the understanding of the mechanism of generation of various luminescence peaks in ZnO bulk single crystals have been made through detailed analysis of photoluminescence (PL) spectra. Nevertheless, there are some disadvantages associated with the use of PL, including a low lateral resolution of $1\mu\text{m}$, which presents a challenge in analysing the nanoscale properties of ZnO. To address this problem, researchers have employed ZnO nanowires, which, however, exhibit a single broad luminescence peak at ambient temperature. This limits the ability to obtain comprehensive data regarding the detailed impurity related recombination processes which are apparent in the low temperature studies of bulk crystals [17].

Other techniques with significant potential include cathodoluminescence (CL). It has been demonstrated to be an invaluable tool for luminescence mapping and is capable of spot analysis of nanoscale objects such as nanowires, with a resolution beyond what is achievable with PL. These developments in the understanding of the luminescence behaviour of ZnO thus indicate its potential utility in the fabrication of short-wavelength photonic devices, which are indispensable components in contemporary optical systems. [18].

3. Field Emission

Field emission represents a highly efficient process of electron emission that is not subject to time delay and which consumes very little power. As a consequence, it constitutes a key technology in a variety of applications. This phenomenon is employed

in numerous electron sources, particularly in vacuum electronics, where large-area addressable field emitter arrays are frequently utilised. Such arrays are integral to a number of devices, including imaging detectors, sources of terahertz and X-ray radiation, and field emission displays. Zinc oxide has emerged as a promising material for field emission cathodes, offering a wide band gap, negative electron affinity, and stable physicochemical properties, which collectively make it an ideal candidate for this application [19].

2.3 Diverse Forms

Zinc oxide is a material of significant importance due to its tendency to exist in the hexagonal wurtzite structure. The majority of research is focused on the control of the crystal growth of ZnO to influence its microstructure and, in particular, the formation of one-dimensional (1D) nanostructures. A variety of organic molecules, including diamines, surfactants and citrate anions, have been employed extensively to regulate the morphology of ZnO and thereby produce a diverse range of nanostructures [20].

These nanostructures exhibit high sensitivity with respect to sonication time, a parameter that is regarded as a crucial determinant in the formation process of these nanostructures. Furthermore, structural analysis has confirmed that ZnO nanorods are single crystalline and retain the hexagonal wurtzite structure. Free-standing single-crystal nanorods of zinc oxide can be produced through a self-coiling mechanism during the growth of polar nanobelts. This phenomenon appears to be regulated by long-range electrostatic interactions that prompt the circular folding of a nanobelt. Consequently, the nanobelt, which continues to coil in a coaxial and uniradial fashion in a loop-by-loop manner, a complete nanoring is created. The loops within the ring are chemically bonded at the local level, which results in a single-crystal structure [21].

ZnO has been synthesised based on its dimensionality, which can be one dimensional (1D), two dimensional (2D), or three dimensional (3D), and exhibits differential properties and applications. The largest of these structures is the one-dimensional variety, which includes shapes such as nanorods, nanoneedles, nanohelices, nanosprings, nanorings, nanoribbons, nanotubes, nanobelts, nanowires and

nanocombs. These structures can be precisely controlled through the careful control of conditions during synthesis [20, 22].

In addition to one-dimensional structures, ZnO has also been synthesised into 2D structure such as nanoplatelets, nanosheets, and nanopellets which have different characteristics. Furthermore, due to the ability to grow complex 3D structures, the field of application of ZnO is even broader [20].

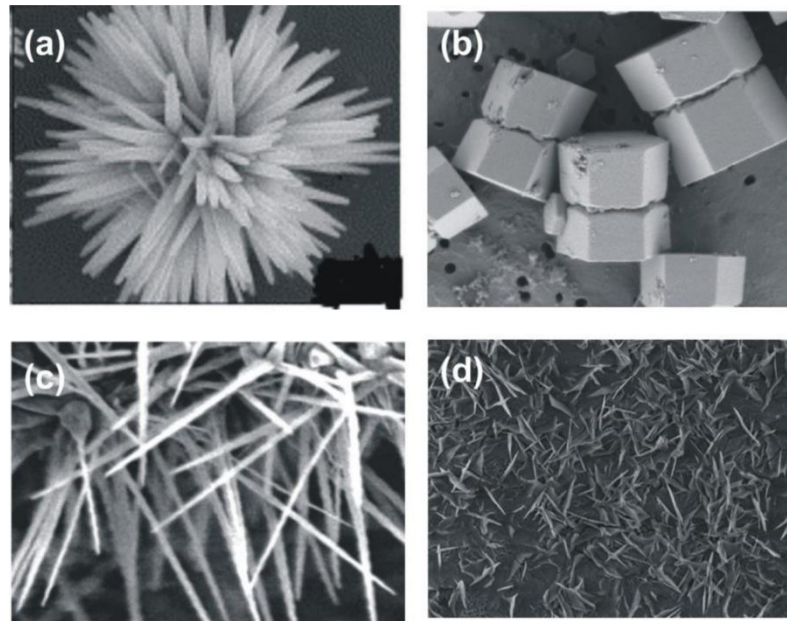


Figure 1: *Examples of zinc oxide structures: a) flower, b) rods, c), d) wires. Created based on [23, 24, 25].*

3. ZnO Nanorods

Among all nanomaterials, zinc oxide nanorods have attracted considerable attention in the field of nanotechnology due to its unique structure, optical and electrical characteristics, which render them suitable for advanced applications. ZnO nanorods possess a wurtzite structure, a hexagonal structure that enhances to the stability of the compound in a variety of conditions [26].

While extensive study and utilisation have been conducted on bulk ZnO, the development of ZnO nanorods has opened up new avenues in the field of nanotechnology. Due to their nanoscale dimensions and high surface area, ZnO nanorods are well-suited for high-tech applications that require enhanced reactivity, sensitivity, and optical performance. These differences provide a rationale for the significant interest in ZnO nanorods in cutting-edge research and development in nanotechnology and materials science [20].

3.1 Difference between ZnO and ZnO Nanorods

Zinc oxide and ZnO nanorods are essentially identical in terms of their chemical composition. However, they exhibit significant differences in their physical structure, size, and the properties that result from these differences.

Bulk ZnO is the conventional form of the material, which is typically found in the following forms: as powders, crystals, or thin films. The particles that constitute bulk ZnO are typically much larger, often measuring in the micrometre range. The larger particle size contributes to the material's stability. ZnO nanorods represent a nanostructured form of ZnO, characterised by their rod-like morphology. The diameters of these nanorods range from a few nanometres to hundreds of nanometres, while their lengths extend up to several micrometres. The high aspect ratio (length-to-diameter ratio) of ZnO nanorods is a key feature that differentiates them from bulk ZnO. The nanoscale size and unique shape result in a much higher surface area-to-volume ratio, which significantly alters their physical and chemical behaviour [1, 20, 25].

ZnO nanorods are distinct from the bulk ZnO in that they exhibit nanoscale dimensions. The larger surface area to volume ratio of ZnO nanorods renders them more chemically

active than other structures, rendering them more suitable for applications such as gas sensing and photocatalysis [20]. Moreover, ZnO nanorods exhibit the enhanced optical properties, namely amplified photoluminescence, this is due to quantum confinement effects [27]. Additionally, these nanorods display higher electrical conductivity, which is a significant factor for applications in nanoelectronics and optoelectronics [28].

3.2 Mechanical, Chemical and Optical Properties

ZnO nanorods are additionally characterised by their notable mechanical properties. They exhibit a high Young's modulus, which is the quantitative measure of the material's stiffness. This mechanical stability is related to the high covalent bonding in the ZnO crystal lattice. It has been demonstrated that ZnO nanorods are capable of withstanding considerable mechanical stress without deformation, rendering them well-suited for utilisation in nanoelectromechanical systems and as reinforcing agents in composite materials [24].

In addition, because the wurtzite crystal structure of ZnO does not have inversion symmetry, the ZnO nanorods have very high piezoelectric properties. These properties enable ZnO nanorods to generate an electrical charge in response to mechanical stress. This makes them suitable for use in energy conversion devices and sensors. Due to its chemical stability, high mechanical strength and piezoelectricity ZnO nanorods are ideal for use in enhanced technological purposes [29].

ZnO nanorods have a number of remarkable chemical properties that make them particularly useful in a wide range of applications. One of the most significant characteristics is their high chemical stability. In addition, due to their resistance to oxidation and corrosion, ZnO nanorods can be engineered to withstand a variety of chemical environments. Most of this stability is due to the strong ZnO covalent bond found in the wurtzite crystal structure, which makes the material difficult to degrade [24].

Furthermore, the photocatalytic activity of ZnO nanorods is considerable, due to the relatively large band gap. It can generate electron-hole pairs when it acts as a photoanode under UV light. These electron-hole pairs can participate in redox reactions.

As a result, ZnO nanorods are extensively used in photocatalysis, mainly for the degradation of organic pollutants in aqueous and gaseous environments, and for the generation of hydrogen by water splitting [30].

In addition, ZnO nanorods have a good capacity for selective adsorption, which is essential for gas sensing. The surface chemistry of ZnO can be modified through functionalisation with a range of organic or inorganic molecules, thereby enhancing its selectivity and sensitivity towards specific gases. For example, when ZnO is doped with other elements or its surface is coated with metals, the reactivity of ZnO towards gases such as NO₂ is significantly different and the sensing properties of the material are improved. A significant characteristic of such materials is that they exhibit high ultraviolet (UV) adsorption, as well as photoluminescence [20, 27].

The wide bandgap enables ZnO nanorods to absorb UV light with high efficiency, making them ideal for use in UV photodetectors and light-emitting diodes (LEDs). In addition, the high exciton binding energy (~60 meV) at room temperature enhances the photoluminescence efficiency of ZnO nanorods, which is a crucial factor for their performance in optoelectronic devices [27].

3.3 Applications and Future Perspectives

One of the most promising applications for which ZnO nanorods have been postulated is in the field of gas sensing. Due to their high surface-to-volume ratio and the capacity to adsorb gas molecules across the surface, they exhibit a high degree of sensitivity to changes in the surrounding environment. For example, ZnO nanorods have demonstrated exceptional capabilities in the detection of gases such as nitrogen dioxide (NO₂) and carbon monoxide (CO). These sensors work on the principle of resistance variation in the ZnO nanorods which is influenced by the adsorption of gas molecules on the nanorods' surface. The interaction frequently involves the adsorption of oxygen molecules, which removes electrons from the ZnO conduction band, resulting in a measurable change in resistance. The sensitivity of these sensors can be precisely calibrated by modifying the nanorods' crystallite size and the operational temperature [29].

In addition to their application in gas sensing, ZnO nanorods are of significance for the fabrication of optoelectronic devices, such as UV photodetectors and LEDs. These materials possess a wide bandgap and a high binding energy of the excitons, making them suitable for use in the aforementioned applications, where they are employed to convert light into electrical energy or vice versa. Furthermore, ZnO nanorods are utilised in photocatalytic processes, particularly in the environmental field, for the degradation of organic pollutants and the production of hydrogen. The ability of these materials to generate electron-hole pairs under UV irradiation in combination with the high surface reactivity makes possible the attainment of highly effective catalytic processes [30].

ZnO nanorods are also used frequently in environmental applications, mainly photocatalytic reactions and the purification of water and air. The materials have the capacity to effectively degrade organic pollutants, a process that is initiated by the generation of reactive oxygen species when the materials are exposed to UV light. Moreover, ZnO nanorods are currently being investigated for their potential in hydrogen production via photocatalytic water splitting. It is hypothesised that they will act as highly efficient catalysts due to their large surface area and high reactivity [31].

Due to its biocompatibility and antimicrobial activity, ZnO nanorods have been considered for application in numerous areas of biomedical engineering including, drug delivery, bioimaging and antibacterial coatings. Their ability to interact with biological systems with relative low toxicity makes them an attractive candidate for incorporation into medical devices [32].

Further research of ZnO nanorods continues due to the potential of improving the properties of these structures and increasing the roles of their utilization. The ongoing advancement of synthesis techniques, including the utilisation of pulsed laser ablation and microwave-assisted methods, is enhancing the quality and uniformity of ZnO nanorods, thereby rendering them increasingly suitable for high-performance applications in sensors, energy harvesting, and nanoelectronics [33].

4. Substrate Selection and Seed Layer Deposition

The growth of ZnO nanorods depends on the deposition of a seed layer, on which the nanorods develop. The seed layer, which may be deposited using a variety of methods, plays a pivotal role in determining the orientation, density, and uniformity of the ZnO nanorods [34].

4.1 Substrate Selection

The choice of substrate is a fundamental aspect of ZnO nanorod fabrication, as it significantly impacts the growth characteristics and overall quality of the resulting structures. In this study, we selected silicon and glass as the primary substrates due to their unique properties that make them well-suited for supporting the growth of ZnO nanorods.

Silicon (Si) is a key material in nanotechnology and semiconductor fields due to its excellent heat resistance and smooth surface, both of which are crucial for growing uniform nanorods. Glass, known for its optical transparency and thermal resistance, was chosen as an additional substrate. Its smooth surface helps ensure uniform deposition of ZnO nanorods, making it especially useful for applications where optical performance is essential, such as in UV photodetectors and LEDs [35].

4.2 Seed Layer Deposition

The deposition of a seed layer is a critical phase in the fabrication of ZnO nanorods, directly influencing their nucleation, growth orientation, and density. Magnetron sputtering is the most common technique used for this purpose. It is a physical vapour deposition method that is highly regarded for its capacity to produce uniform and adherent thin films on a diverse range of substrates, including silicon and glass [36].

4.1.1 Magnetron Sputtering

In the process of magnetron sputtering, a target material (in this case, ZnO) is subjected to bombardment by high-energy ions within a vacuum chamber. The ions are usually generated in a plasma and when they collide with the surface of the substrate, atoms are dislodged and then deposited onto a substrate thus forming a thin film or seed layer. Technique of magnetron sputtering is used for deposited ZnO on two types of

substrates: silicon (Si) and glass. Magnetron sputtering technique is used for deposited ZnO on two substrates silicon (Si) and glass [37].

The numerous advantages of this technology make it suitable for a variety of high-tech applications. The principal advantage of magnetron sputtering is its capacity to generate uniform thin films of a uniform thickness on a substrate. This is very crucial especially in applications where precise control of the characteristics of the deposited film is required [38]. The thin films produced by magnetron sputtering are typically characterised by excellent adhesion to the substrate, which is a significant advantage for the durability of the films in a multitude of applications. Magnetron sputtering is often combined with other deposition techniques, such as radio frequency sputtering, frequently results in the formation of highly purified films and crystalline structures of exceptional quality. This high film quality is essential for applications in the fields of electronics and optics [39].

The versatility of magnetron sputtering is evidenced by the range of materials that can be deposited, including metals, semiconductors, and dielectrics. In addition, it can be employed to create multi-layered structures and complex film compositions, thereby facilitating the development of advanced materials for a diverse range of applications. The process allows for precise control over both the thickness of the film and its composition, enabling the design of material properties to meet specific requirements. This control is of great significance for a number of fields, including microelectronics, optics, sensors, and other areas of application. In comparison to alternative deposition techniques such as thermal evaporation, magnetron sputtering works at relatively low substrate temperatures which is of significance in coating temperature sensitive components [37].

However, there are several disadvantages associated with this technique that may impact its suitability for a given application. One of the primary disadvantages of magnetron sputtering is the initial cost of the required equipment, which includes a vacuum chamber, a magnetron source, and power supplies. Magnetron sputtering uses a complex equipment that requires frequent tuning and maintenance. However, problems like target poisoning, which is the development of non-conductive layers on

the target surface, may lead to low efficiency and requires frequent cleaning of the target or replacement of the parts [39].

Compared to other deposition techniques, magnetron sputtering often has a slower deposition rate, leading to longer deposition times, especially for thicker films. This can potentially reduce the overall output rate in industrial applications. Despite these challenges, magnetron sputtering generally maintains high uniformity, ensuring that parameters such as film thickness remain consistent across the substrate. However, achieving uniformity on very large substrates can still be problematic, potentially leading to variations in film properties across different areas of the substrate. The process involves ion bombardment, which has the potential to introduce stress and defects into the film. Such effects may affect the strength of the film, and this may be a serious concern in areas where the substrates are easily damageable or where high precision is required. In comparison to other deposition techniques, sputtering is less material efficient. The target material is not entirely deposited on the substrate, which results in a considerable loss of material. It also can lead to unwanted heating of the substrate which can be undesirable for the heat-sensitive materials. In addition, this heating can affect the film's crystallography and may introduce stress or phase transformations [37, 39].

4.1.2. Alternative Deposition Techniques

Despite the fact that magnetron sputtering is a technique with a long and well-documented history of use, there are a number of alternative approaches to seed layer deposition which offer a number of advantages depending on the specific requirements of a particular application.

The sol-gel method is a chemical process in which a solution transitions to a solid gel phase. In the case of zinc oxide seed layers, the typical method for preparing the precursor solution involves the dissolution of zinc acetate or zinc nitrate in a suitable solvent, followed by a series of hydrolysis and condensation reactions. Subsequently, the resulting gel is applied to the substrate and subjected to a heat treatment, thus forming the seed layer. This method is economically viable. The sol-gel process is relatively inexpensive and does not require the use of sophisticated equipment. The

process is straightforward and can be readily adapted for use with larger substrates. The method is also versatile. The use of different precursor chemicals allows for flexibility in the tailoring of the properties of the seed layer. Nevertheless, the sol-gel method may not attain the same degree of uniformity and adhesion as sputtering, which can impact the quality of the resulting nanorods [40].

Chemical Bath Deposition (CBD) involves the immersion of the substrate in a bath containing a chemical solution comprising zinc salts and other reagents. The deposition is the result of a chemical reaction that forms a thin layer of ZnO on the substrate. This method is advantageous for the following reasons.

The method is also cost-effective, requiring only minimal equipment and implementation. Furthermore, the method is scalable. This method is particularly suited to the deposition of materials on large-area substrates, making it an ideal choice for applications where uniform coverage is a prerequisite. The deposition process occurs at a relatively low temperature. The process can be conducted at relatively low temperatures, which is advantageous for substrates that are sensitive to heat. The principal disadvantage of CBD is the possibility of non-uniform layers, which may result in inconsistent nanorod growth [41].

Pulsed laser deposition (PLD) is a process in which a high-power laser is employed to remove material from a ZnO target and subsequently deposit it onto a substrate to form a seed layer. This technique offers several advantages. It provides high accuracy; it can be employed in a diverse range of applications and enables the production of thin layers with a specific composition ratio. Additionally, the process generally produces films with high purity, which is beneficial for electronic applications. However, PLD is relatively expensive and requires sophisticated equipment, which may limit its use to specialized applications [42].

4.3 Thermal Annealing

Thermal annealing represents a pivotal post-deposition process in the field of materials science, particularly in the context of the fabrication of nanostructures such as ZnO nanorods. The process entails subjecting the material to a specific temperature for a defined period before allowing it to cool at a gradual rate. The controlled heating and

cooling process can exert a significant influence on the microstructural, mechanical, and electrical properties of the material. In the case of ZnO nanorods, annealing is frequently employed with the objective of enhancing crystallinity, reducing defects and improving the overall performance of the material [43].

The role of thermal annealing in the improvement of crystallinity is a crucial aspect of material science. The process of annealing facilitates the reorientation of atoms within a given material, enabling them to adopt a more stable and lower-energy configuration. This process enhances the crystallinity of ZnO nanorods, leading to the formation of more defined crystal structures, which is significant for applications in electronics and photonics [44]. The annealing process also serves to reduce the probability of the occurrence of defects. During the annealing process, the occurrence of defects, including dislocations, vacancies, and grain boundaries, can be reduced or even eliminated in the ZnO nanorods. The reduction in defects has the effect of enhancing the electrical and optical properties of the nanorods, leading to an improvement in their efficiency in devices such as sensors and UV photodetectors. The annealing process can also serve to relieve internal stresses that may have developed during the deposition or growth of the ZnO nanorods. Furthermore, the annealing process can also serve to relieve the internal stresses that emerge during the deposition or growth of ZnO nanorods. By reducing these stresses, the mechanical integrity of the nanorods is enhanced, which is of great importance for applications that necessitate mechanical stability [45].

Annealing has the potential to enhance the conductivity and optical transparency of ZnO nanorods, which is especially advantageous for applications in optoelectronics, where high transparency and conductivity are essential. [43].

4.2.1 Advantages and Disadvantages of Annealed and Non-Annealed Samples

The advantages of annealed samples include enhanced crystallinity. The crystallinity of annealed samples is higher, which is directly correlated with enhanced electronic and optical properties. This renders them more appropriate for high-performance applications [44].

A reduction in the density of defects is also observed. The process has the effect of significantly reducing the number of structural defects, which have the potential to trap carriers and thereby impair the efficiency of devices such as LEDs and solar cells. Improved stability is another advantage of annealed samples. The annealed ZnO nanorods display enhanced chemical and thermal stability, thereby improving their durability in a range of environments. The electrical performance of annealed samples is typically enhanced due to the reduction in defects and improvement in crystallinity, which leads to a decrease in resistance and an increase in carrier mobility [46].

The disadvantages of annealed samples include an increased level of process complexity. The addition of the annealing process introduces an additional step to the fabrication process, which in turn increases the overall complexity and production time. The potential for grain growth is a further consideration. Although annealing is an effective method for reducing defects, it can also result in the unintended growth of grains, which may affect the desired properties of the nanorods.

Thermal stress is a type of stress that occurs when heat energy is applied to a material, causing the material to generate internal stress. It is important to maintain control over thermal cycling, which is typical for annealing, as the process may cause the appearance of new stresses that can lead to the appearance of cracks in some materials [45].

The advantages of non-annealed samples include a simpler fabrication process. The fabrication process is simplified, accelerated and less expensive as a result of the elimination of the annealing stage. The retention of nanoscale features is a further advantage of non-annealed samples. It is possible that non-annealed samples may better retain their original nanostructure, which could be advantageous for certain applications where small grain sizes are desired. The avoidance of thermal damage is a further advantage. Some materials are susceptible to thermal degradation when subjected to high-temperature annealing, resulting in undesirable alterations or loss of functionality. The risk of such damage is avoided by the use of non-annealed samples [43].

The disadvantages of non-annealed samples include a higher defect density. Non-annealed samples typically display a greater concentration of defects, which can impede the flow of charge carriers and, in turn, lead to a reduction in device performance. The absence of thermal treatment results in non-annealed samples exhibiting reduced crystallinity, which in turn leads to inferior electronic and optical properties. The lack of thermal treatment results in non-annealed samples exhibiting reduced chemical and thermal stability, which consequently leads to a reduction in durability when subjected to long-term applications [46].

5 Hydrothermal Synthesis

Hydrothermal synthesis is a technique that is widely employed in materials science for the preparation of a variety of nanomaterials, including zinc oxide nanorods. This method entails the chemical reaction of precursors in an aqueous solution at elevated temperatures and pressures. The process replicates the natural geological conditions that facilitate the formation of minerals, making it an effective method for synthesising crystalline materials with high purity and controlled morphology. [47].

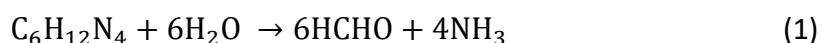
In hydrothermal synthesis, the basic process involves dissolving precursors in water, which acts as both a solvent and a reaction medium. The solution is then heated above its boiling point, resulting in increased pressure within the sealed flask. Under these conditions, the reactants undergo a series of nucleation and growth processes, resulting in the formation of the desired crystalline material [1,2].

For ZnO nanorods, a typical hydrothermal synthesis uses hexamethylenetetramine (HMTA) and zinc acetate as precursors:

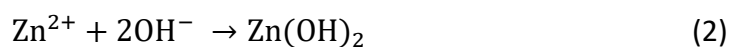
1. Reaction Mechanism

The reaction mechanism in hydrothermal synthesis involves complex chemical processes that are influenced by the specific reactants, temperature, pressure, and duration of the reaction. Understanding this mechanism is key to optimizing the synthesis of ZnO nanorods with desired properties.

HMTA ($C_6H_{12}N_4$) decomposes under hydrothermal conditions, releasing formaldehyde (HCHO) and ammonia (NH_3):



In the hydrothermal synthesis, zinc acetate functions as the zinc precursor. Upon dissolution in water, the compound dissociates into zinc ions (Zn^{2+}) and acetate ions (CH_3COO^-). The released ammonia reacts with zinc acetate in the solution to form zinc hydroxide:



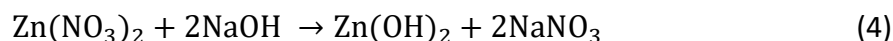
On further heating, zinc hydroxide dehydrates to form ZnO:



This process produces ZnO nanorods with controlled dimensions and high purity [10].

2. Alternative Chemistries

Another common precursor used in hydrothermal synthesis is zinc nitrate ($\text{Zn}(\text{NO}_3)_2$). In this process, zinc nitrate reacts with a base (such as NaOH) under hydrothermal conditions:



The subsequent dehydration of the zinc hydroxide forms ZnO:



Zinc acetate or zinc nitrate can also react with ammonium hydroxide, another common method, to form ZnO through similar hydrothermal reactions [48].

5.1 Advantages and Disadvantages

The advantages of hydrothermal synthesis include the ability to control the morphology of the resulting nanomaterials. This is achieved through precise control over the size, shape, and crystallinity of the nanomaterials. This is of particular significance in contexts where the formation of specific nanostructures, such as rods, wires, or spheres, is necessary. The resulting product has high purity. The process is conducted at a relatively low temperature. In comparison to alternative synthesis techniques, such as chemical vapor deposition (CVD) or solid-state reactions, hydrothermal synthesis is conducted at relatively low temperatures. This has the effect of reducing both energy consumption and costs. The scalability of this process is an additional advantage. This method is scalable and can be employed to produce materials in large quantities, rendering it suitable for industrial applications. Hydrothermal synthesis is a versatile method that can be applied to a wide range of materials, including oxides, sulfides, and other inorganic compounds [49].

The disadvantages of hydrothermal synthesis include: the necessity for lengthy reaction times is another disadvantage of this method. Hydrothermal processes frequently necessitate prolonged reaction times, which can span several hours to days, and may thus impede overall productivity. A further disadvantage is the limited temperature

range. The process is typically constrained to temperatures below 350°C, which may prove inadequate for the synthesis of certain high-temperature phases. Batch processing is a method of conducting a chemical reaction in a single vessel, whereby the contents are transferred to a second vessel at the end of the reaction. Hydrothermal synthesis is typically conducted in a batch process, which may prove less efficient than continuous processing techniques [49,50].

5.2 Comparison with Other Synthesis Methods

1. Sol-gel Process:

In contrast to the hydrothermal synthesis process, the sol-gel process entails the transformation of a system from a liquid "sol" into a solid "gel" phase. Although the sol-gel process offers the advantage of producing thin films and coatings, it often necessitates higher temperatures for crystallisation and does not provide the same degree of control over nanostructures as is afforded by hydrothermal synthesis. Hydrothermal synthesis affords superior control over nanostructures and material purity due to the sealed, high-pressure environment, which minimises contamination and allows for precise adjustment of material properties. In contrast, the sol-gel method, while effective for producing thin films and coatings, often lacks the same level of control over nanostructure uniformity and may require additional processing to achieve the desired degree of crystallinity [51]. Hydrothermal synthesis necessitates the use of high temperatures and pressures, which in turn requires the utilisation of specialised equipment and contributes to elevated operational costs. In contrast, the sol-gel method commences with low-temperature reactions, which can be beneficial for the processing of heat-sensitive substrates. Nevertheless, the sol-gel method frequently necessitates subsequent high-temperature treatments to attain material crystallisation, which can negate some of its initial benefits. Both methods are versatile, but they excel in different areas. Hydrothermal synthesis is well-suited for creating complex crystalline materials with high purity, making it ideal for applications requiring precise nanostructures and high-performance materials. The sol-gel method is advantageous for producing thin films and coatings with controlled composition and uniformity, making it suitable for applications in electronics, optics, and catalysis [52].

2. Chemical Vapor Deposition (CVD):

CVD is a high-temperature process that yields high-quality films and nanostructures with excellent crystallinity. However, the necessity for complex equipment and a high energy input renders it less economical and versatile in comparison to hydrothermal synthesis. CVD is an effective method for producing high-quality films with excellent crystallinity and uniformity. However, the complexity of the equipment and process can present challenges in maintaining consistent purity and control. In contrast to hydrothermal synthesis, CVD requires high-temperature conditions within a vacuum chamber, resulting in significant energy consumption [53].

3. Precipitation method:

The precipitation method is a straightforward and economical approach that involves the formation of solid particles through the mixing of solutions. Nevertheless, this method frequently lacks the precision in controlling particle size and shape that hydrothermal synthesis affords. The precipitation method is a simpler and more cost-effective alternative, though it may lack the fine control over particle characteristics and require additional processing steps to improve purity and uniformity [54].

4. Electrochemical Deposition:

Electrochemical deposition is a method that enables the deposition of materials onto a conductive substrate through the application of an electric potential. Although it can produce high-quality coatings, it is less effective than hydrothermal synthesis in producing uniform, high-purity nanostructures. Electrochemical deposition operates at relatively lower temperatures and is simpler in terms of equipment, which makes it cost-effective and suitable for large-scale applications. However, precise control over current and solution composition may be required to achieve the desired results. Electrochemical deposition is particularly effective for producing high-quality metal coatings and is advantageous for applications requiring detailed patterning and localised deposition. However, its application is generally limited to metals and conductive materials [55].

6 Scanning Electron Microscope (SEM)

Scanning Electron Microscopy (SEM) is an indispensable instrument for the characterisation of nanomaterials, providing high-resolution imaging that is pivotal for elucidating the structural and morphological attributes of materials such as zinc oxide nanorods [56].

SEM is a technique that employs a focused beam of electrons to scan the surface of a sample. The electrons interact with the atoms in the sample, resulting in the generation of signals that can be detected and subsequently translated into high-resolution images. The principal signals utilised in SEM encompass secondary electrons (SE), backscattered electrons (BSE), and X-rays. Each of these provides distinct insights into the sample's surface topography, composition, and crystallography [57].

The SEM is instrumental in providing detailed images of the surface of the ZnO nanorods, which reveal their shape, size, and uniformity. ZnO nanorods typically exhibit a hexagonal cross-section, and SEM images allow for precise measurement of their diameter and length, which are crucial parameters for their application in electronics and photonics [56].

The presence of surface defects, including dislocations, grain boundaries, and surface roughness, can have a considerable impact on the properties of ZnO nanorods. The high-resolution images produced by SEM facilitate the identification of defects, thereby enabling the optimisation of synthesis parameters to produce high-quality nanorods with fewer imperfections. While SEM primarily provides morphological information, it can be coupled with Energy Dispersive X-ray Spectroscopy (EDS) to perform elemental analysis. This capability is particularly useful for detecting impurities or dopants within ZnO nanorods, which can influence their electronic and optical properties [56].

6.1 Advantages and Limitations

The capacity to capture detailed images is a significant advantage of this technique. The use of SEM allows for the capture of images at the nanometre scale, which is essential for the observation of the intricate details of ZnO nanorods. This level of resolution allows for the visualisation of surface features, grain boundaries, and defects, which are

critical for understanding the material's properties and behaviour. The capacity to generate comprehensive surface topography enables researchers to discern growth patterns, structural integrity, and overall morphology in ZnO nanorods, thereby furnishing insights that are pivotal for optimising their synthesis and application. The versatility of the method is evidenced by the wide range of materials that can be utilised. The versatility of the SEM allows it to be used on a wide range of materials, including metals, polymers, ceramics, and semiconductors such as ZnO nanorods. This renders it a valuable instrument for interdisciplinary research, in which ZnO nanorods may constitute a component of a composite material or a hybrid structure. Compositional analysis is a valuable tool for investigating the chemical composition of materials. When used in conjunction with Energy Dispersive X-ray Spectroscopy, SEM can facilitate elemental analysis, which is advantageous for the detection of impurities, dopants, or other elements that may be present in ZnO nanorods. This is of particular importance in applications where the purity and composition of the material in question directly affect its performance [56,57].

There are certain limitations to the procedure. One such limitation is the requirement for a certain level of conductivity. One of the principal constraints associated with SEM is the necessity for conductive samples. Due to their semiconductor nature, ZnO nanorods frequently necessitate the application of a conductive coating (such as gold or carbon) prior to imaging. This can potentially result in the obfuscation of certain surface details or the alteration of the sample's intrinsic state [56].

A vacuum environment is required. The vacuum environment in which SEM operates may present limitations with regard to the types of samples that can be analysed. For instance, samples comprising volatile components or exhibiting sensitivity to vacuum conditions may undergo degradation or alteration during analysis. The degree to which the surface of a sample is sensitive to the analysis process [58].

The penetration depth of the electron beam is limited. A fundamental aspect of the SEM is that it provides information about the surface of the sample. The electron penetration depth is typically limited to a few nanometres. This indicates that SEM is unable to

provide information regarding the internal structure of ZnO nanorods, which could be crucial for specific applications [57].

The potential for radiation damage must also be considered. The interaction of the electron beam with the sample is a crucial aspect of the SEM process. The high-energy electron beam utilised in SEM has the potential to cause radiation damage to materials of a sensitive nature, including ZnO nanorods. Prolonged exposure can result in heating, charging, or even the destruction of the nanorods, particularly if they are not sufficiently conductive or stable under the beam [58].

7 Experimental Preparation and Methodology

This chapter provides a detailed account of the preparation made in the hydrothermal synthesis of zinc oxide nanorods. It focuses on the methodologies employed, the equipment and chemicals used, and the experimental adjustments made during the process. The synthesis was designed to optimise the growth of ZnO nanorods by fine-tuning various parameters, thereby ensuring the consistency and quality of the nanostructures produced.

7.1 Chemicals

The synthesis was conducted using zinc acetate and hexamethylenetetramine, with each component fulfilling a specific role in the synthesis.

HMTA functions as a stabilising agent and a weak base. The hydrolysis of HMTA in water is a slow process, producing formaldehyde and ammonia. The ammonia generated increases the pH of the solution, leading to the formation of hydroxide ions (OH^-), which then react with zinc ions to form ZnO. Furthermore, HMTA regulates the rate of ZnO formation, influencing the growth and orientation of the nanorods. Its slow decomposition ensures a controlled and gradual supply of hydroxide ions, promoting the uniform growth of ZnO nanorods [59].

Deionised water plays a crucial role in the synthesis process, acting as the solvent. It is essential to use high-purity water to avoid the introduction of extraneous ions or contaminants, which could interfere with the nucleation and growth processes. The purity of the water ensures consistent reaction conditions and contributes to the reproducibility of the synthesis [59].

7.2 Equipment

It is evident that the efficacy of the hydrothermal synthesis process is contingent upon the precision and control afforded by the apparatus employed. The following equipment is indispensable for maintaining the specific conditions required for the growth of ZnO nanorods. Several key pieces of equipment were used in the synthesis process:

1. Magnetic stirrer with heating functionality (IKA RCT Digital Series):

The magnetic stirrer with heating capabilities is a crucial piece of equipment, as it ensures uniform mixing and consistent heating of the reaction mixture. It is imperative to exercise precise control over the stirring speed and temperature in order to maintain homogeneity in the solution, which directly affects the quality and uniformity of the ZnO nanorods. The IKA RCT Digital Series, for instance, enables precise calibration of these variables, rendering it an optimal choice for controlled hydrothermal synthesis.

2. Ultrasonic Cleaner (Elmasonic P):

Initially, an ultrasonic cleaner was used to improve the dispersion of the reactants in the solution. The ultrasonic waves generated by the cleaner help to break up any aggregates and ensure thorough mixing of the chemical precursors. However, the use of the ultrasonic cleaner was later discontinued because it inadvertently heated the solution, which could lead to uncontrolled temperature fluctuations and consequently inconsistent nanorod growth.

3. Custom-Built Apparatus for Substrate Holding:

A custom designed apparatus was developed to securely hold the substrates during the hydrothermal synthesis process. This apparatus was designed to prevent the substrates from contacting the walls of the reaction vessel, which could lead to uneven growth of the nanorods. The apparatus also included features to minimise evaporation of the solution during the high-temperature synthesis, thereby maintaining consistent reaction conditions throughout the process.

4. Drying Equipment (Nitrogen Dryer):

After the synthesis is complete, the ZnO nanorods are dried using a nitrogen stream. The use of nitrogen prevents oxidation and contamination of the nanorods during the drying process, helping to preserve their structural and chemical integrity. This step is essential for maintaining the quality of the nanorods before further characterization or use in applications.

5. Temperature Probe and Monitoring System:

Accurate temperature monitoring is essential during the hydrothermal synthesis process. A temperature probe, inserted through a small hole in the aluminum foil covering the reaction flask, ensures that the temperature is maintained at the desired level throughout the experiment. Consistent temperature control is vital for regulating the growth rate and size of the ZnO nanorods.

7.3 Substrate and Seed Layer

The choice of substrate and the application of a ZnO seed layer are critical factors in the successful synthesis of ZnO nanorods.

The experiments primarily employed two distinct types of substrates: silicon (Si) and glass. Silicon substrates were selected for their crystalline structure, which provides an optimal lattice match for ZnO, facilitating uniform and controlled growth of nanorods. The excellent thermal conductivity of silicon also allows for high-temperature processing, which is crucial for achieving well-defined nanorods with the desired structural properties [44].

Glass substrates were employed as an alternative to silicon in order to explore the influence of an amorphous substrate on the growth of ZnO nanorods. In contrast to silicon, glass lacks a crystalline structure, which can result in more irregular growth patterns and greater variability in nanorod morphology. However, glass substrates offer certain advantages in applications that require transparency and a lower cost [36].

In this study, the objective was to enhance the growth of ZnO nanorods. A seed layer of ZnO was applied to the substrates. The seed layer functions as a template, providing nucleation sites that align with the crystal structure of the deposited ZnO, thereby facilitating epitaxial growth of the ZnO nanorods. The presence of a ZnO seed layer is particularly advantageous on substrates such as glass, where the absence of a crystalline lattice would otherwise result in poor nucleation and random growth of the nanorods [45].

In addition to using bare substrates, some experiments involved the annealing of both silicon and glass substrates.

7.4 Experimental Setup



Figure 2: *Experimental setup.*

Figure 2 illustrates that the IKA RCT digital magnetic stirrer is situated at the base of the setup. The digital display indicates that the device is set to a temperature of 95°C, with a proportional-integral-derivative (PID) control system regulating the temperature. The chemical flask, constructed from glass, is situated on the upper surface of the magnetic stirrer. The chemical flask is filled with a clear solution containing the requisite chemical precursors for the synthesis. The flask has been constructed in such a way as to be capable of withstanding the elevated temperatures that are typically employed in hydrothermal synthesis. The homogeneous distribution of the liquid within the flask indicates that the necessary conditions for uniform nanorod growth have been met. A custom-built apparatus is visible within the reaction vessel, which is used to hold the substrates on which the ZnO nanorods will grow. The apparatus is constructed from stainless steel, which ensures that it is chemically inert and does not react with the solution. The apparatus is suspended above the base of the vessel, thus preventing contact with the flask walls and ensuring uniform exposure of the substrates to the reactive solution. A temperature probe is inserted into the chemical flask and connected to a temperature monitoring system, which ensures precise thermal control during the synthesis. The probe is covered with aluminium foil and insulation material (a foam

block) in order to minimise heat loss and prevent evaporation, thus maintaining a stable temperature within the vessel. The insulation is of critical importance for maintaining consistent reaction conditions, particularly in syntheses of long duration. The aluminium foil wrapped around the upper portion of the chemical flask fulfils a number of functions. Firstly, it serves to reduce the rate of evaporation. Secondly, it maintains a more consistent temperature within the flask. Thirdly, it prevents contamination from external sources. The small hole for the temperature probe is designed with great care to minimise disruption to the sealed environment.

8 Procedure for Hydrothermal Synthesis

8.1 Initial Experimental Setup and Procedure

The initial three measurements were obtained through the following procedure. A precision laboratory balance was used to weigh 1.756 g of zinc acetate and 1.121 g of hexamethylenetetramine, which were then placed into separate flasks containing 200 mL of deionized water each. Both solutions were subjected to ultrasonic treatment in an ultrasonic cleaner for a period of 15 minutes in order to ensure thorough dissolution and homogeneity of the precursor solutions. Subsequently, the two solutions were combined in a larger flask and subjected to ultrasonic treatment for a further 15 minutes. This step was of great importance in ensuring the uniform distribution of the reactants within the solution.

A substrate holder was positioned on two larger steel nuts within the solution, and a magnetic stir bar was introduced to facilitate agitation. The substrate holder contained four silicon substrates with thin ZnO layer. The upper portion of the flask was wrapped in aluminium foil to minimise evaporation, with a small aperture created to facilitate the insertion of a temperature probe. The temperature was set to 120°C, the stirring speed to 100 rpm, and the reaction time to 2 hours.

The condition of the reaction was monitored at 30-minute intervals, with a final check conducted five minutes before completion. Following the reaction, the apparatus was carefully removed, and the samples were dried using nitrogen gas to preserve the integrity of the ZnO nanorods.

The samples were stored in Petri dishes, labelled according to their respective measurement numbers, and analysed using an electron microscope. However, the initial measurements yielded no positive results, as the ZnO nanorods failed to grow, due to the delamination of the seed layer from the substrate.

8.2 Optimization and Modifications in Subsequent Experiments

On the fourth attempt, it was established that the initial apparatus lacked the requisite stability. Consequently, a series of modifications were introduced.

A redesign of the substrate holder was undertaken. A new holder was constructed, designed to suspend the substrates from the top rather than place them in the flask. Three screws were affixed to the glass rectangular plates that held the substrates, with the central screw being the longest. This allowed for the attachment of a longer rod that was inserted into a thick layer of polystyrene foam.

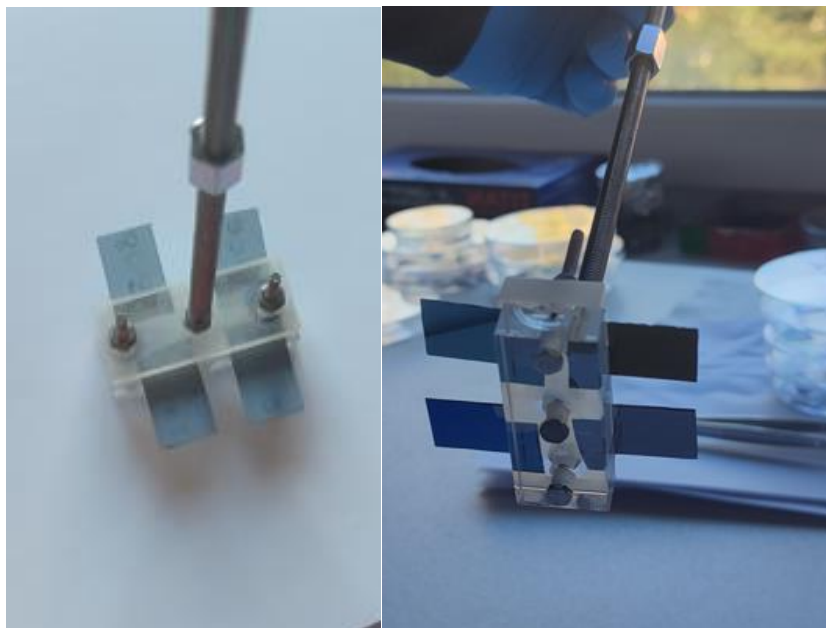


Figure 3: *A redesigned substrate holder.*

The polystyrene was positioned on top of the aluminium foil in order to further reduce evaporation. This design ensured a more stable and consistent environment for the growth of nanorods.

Modifications were also made to the reaction conditions. The magnetic stir bar was left in the solution throughout the synthesis, which resulted in a more homogeneous nanorod layer. Furthermore, it was previously observed that a synthesis time of two hours was excessive, resulting in the delamination of the thin ZnO layer. Accordingly, the reaction time was reduced to 60 minutes.

A modification was made to the mixing technique in subsequent experiments. The use of the ultrasonic cleaner was discontinued due to the unintended heating effect on the solution. Instead, following the combination of the solutions, the mixture was subjected to high-frequency stirring (500-600 rpm) using the magnetic stirrer.

In the fourth set of measurements, the synthesis was initiated with a silicon substrate coated with a thermally annealed ZnO seed layer for comparison with a substrate that did not undergo thermal annealing. The procedure was identical, with the sole difference being the treatment of the ZnO seed layer on the silicon substrate. The same approach was also employed in our fifth and sixth experiments.

8.3 Further Experimental Variations

Subsequent experiment (seventh measurements) was conducted to investigate the influence of stirring frequency on nanorod size and homogeneity. The electron microscope analysis indicated that both measurements yielded comparable results, thereby substantiating the hypothesis that the substrate's underlying layer exerts a pronounced influence on nanorod size.

In the eighth measurement, an alternative substrate was employed. Instead of silicon, a glass substrate was utilised.

In order to evaluate the influence of temperature on the synthesis process, the temperature was varied for the ninth and tenth measurements. The initial temperature was reduced from the standard 90°C to 85°C, and in the subsequent experiment, it was increased to 95°C.

The following chapter will present a detailed analysis of the factors that influenced the synthesis, based on the findings of the aforementioned measurements.

9 Factors Influencing the Growth of Nanorods and Potential Sources of Error

It is reasonable to postulate that the following factors may exert an influence on the growth of nanorods.

9.1 Stirring Frequency

Stirring is of great consequence in maintaining a uniform concentration of reactants within the solution, which can, in turn, influence the growth of nanostructures.

In order to evaluate this, two distinct stirring frequencies were employed during the course of these experiments. Subsequently, the resulting nanorods were analysed using scanning electron microscopy in order to evaluate their size and distribution across the substrates. The SEM images demonstrated that, despite the variation in stirring frequencies, both sets of conditions yielded nanorods of comparable size and homogeneity. This consistency across different stirring rates indicated that, within the tested range, stirring frequency did not have a significant impact on the final nanorod characteristics.

Interestingly, this led to a critical observation that the underlying substrate layer may play a more pivotal role in determining the size of the nanorods than the stirring conditions. The substrate's surface properties, including its crystallinity, roughness, and chemical composition, have the potential to influence nucleation sites and growth kinetics, which in turn may affect nanorod formation to a greater extent than the dynamic conditions within the solution.

9.2 Substrate and Seed Layer

The substrate plays a dual role in the growth of nanorods, providing both physical support and influencing the orientation, density, and uniformity of the nanorods. Several key factors related to the substrate, including the presence and treatment of the seed layer, affect the overall outcome of the synthesis process [44].

In this study, both silicon and glass (with and without thermal annealing) substrates were used to observe and compare the growth behaviours of ZnO nanorods. The results

revealed notable differences in the stability, adhesion, and overall quality of the nanorod arrays depending on the substrate material, the treatment of the substrate, and the associated seed layer.

The following chapter will provide an in-depth analysis of different substrate and their capacity to support the growth of nanorods.

9.3 Temperature

The ninth and tenth experiments were conducted with the objective of investigating the impact of temperature on the hydrothermal synthesis of ZnO nanorods. It is evident that temperature plays a pivotal role in this process, as it exerts a direct influence on reaction rates, the solubility of reactants, and ion diffusion. These factors are of paramount importance for the controlled growth of nanostructures.

The ninth experiment involved a reduction in the synthesis temperature from the standard 90°C to 85°C. The rationale was that a reduction in temperature might result in a slowing of the growth process, which could in turn lead to the formation of nanorods with greater uniformity and control. However, the results demonstrated no significant improvement in the uniformity or size distribution of the nanorods. This outcome indicates that 85°C may not provide sufficient thermal energy to optimise the quality of the nanostructures under the experimental conditions employed.

In contrast, the tenth experiment increased the temperature to 95°C to ascertain whether a greater thermal input could facilitate accelerated growth or enhance the nanorod morphology. The results of the SEM analysis indicated that, while the nanorods were successfully synthesised, there was a slight increase in the size variation. This indicates that elevated temperatures may facilitate accelerated growth, but could also result in increased variability, potentially due to enhanced nucleation rates or fluctuations in reactant solubility.

These findings underscore the complex influence of temperature on hydrothermal synthesis, where both lower and higher temperatures can impede optimal nanorod growth. The results underscore the importance of precise control over the synthesis parameters to achieve the desired nanostructural characteristics.

Another noteworthy observation pertains to the performance of the magnetic stirrer with heating functionality. It was observed that the device did not heat the chemical solutions in a uniform manner or at a consistent rate, which may have introduced additional variability into the synthesis process. The accompanying graph in Figure 4 illustrates the relationship between temperature and time, as observed during our measurements.

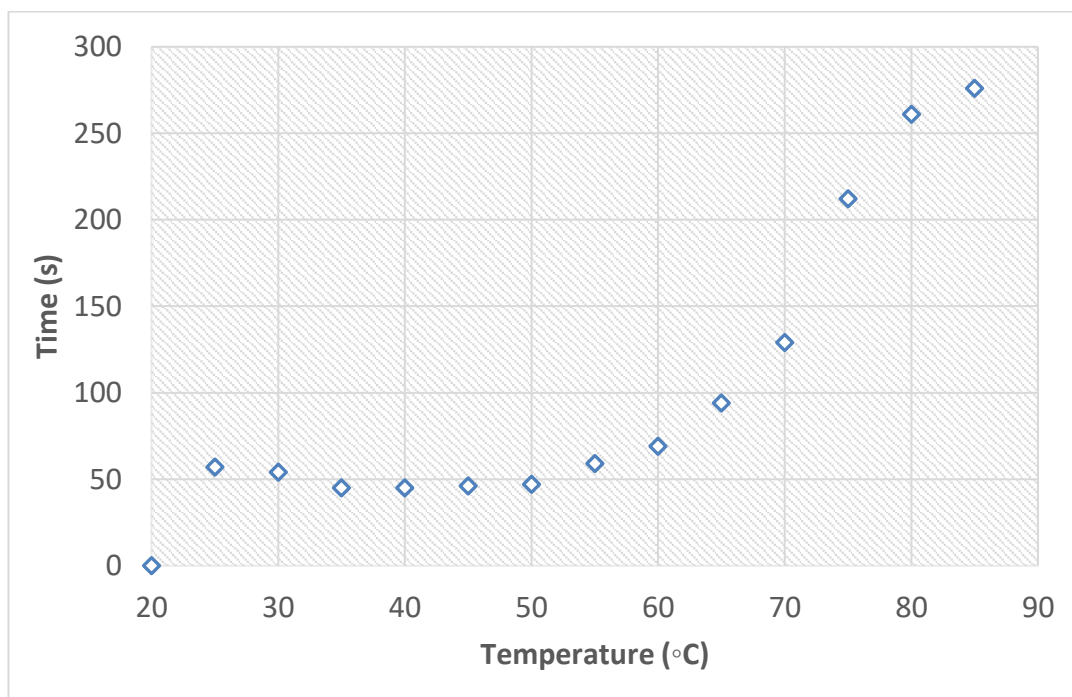


Figure 4: *Dependency of temperature on time during the measurements.*

The experiments demonstrated the necessity for precise control of temperature and substrate conditions to optimise the synthesis of ZnO nanorods. Further work could involve a more systematic exploration of these variables, including finer temperature adjustments and different substrate materials, with the aim of further refining the synthesis process and enhancing the quality of the resulting nanostructures.

9.4 Duration of Process

The duration of the hydrothermal process directly impacts the growth rate of ZnO nanorods. A longer synthesis time generally allows for more extended crystal growth, resulting in longer nanorods. However, there is a balance to be struck, as excessively

long synthesis times can lead to overgrowth, where the nanorods become too long, leading to structural instability and potential detachment from the substrate [8].

In our experiments, it was observed that extending the process duration beyond the optimal time led to the degradation of ZnO nanorods on both silicon and glass substrates, where both were coated with a ZnO thin seed layer.

On the glass substrates, the prolonged synthesis resulted in longer nanorods, but these were increasingly prone to random orientation and structural defects. Although the ZnO seed layer on glass supported initial nanorod growth, it couldn't fully counteract the substrate's amorphous nature, resulting in less uniform and more variable nanorod structures.

On Si substrates with a ZnO seed layer, the crystalline nature of the silicon allowed for more controlled growth initially. However, when the synthesis time was extended, the over-elongated nanorods showed a decrease in uniformity, which could compromise their effectiveness in applications requiring precise nanostructures. Despite the presence of the ZnO seed layer, the extended process time led to nanorods with less consistent dimensions.

The homogeneity and morphology of ZnO nanorods are also significantly affected by the duration of the synthesis process. An optimal synthesis time is crucial for achieving nanorods with uniform diameters and well-defined hexagonal morphologies [1]. In our experiments, it was found that shorter synthesis times often led to less homogeneous nanorods, with greater variability in size and shape. This was more pronounced on glass substrates, where the lack of crystalline structure already posed challenges for uniform growth. As the duration increased, the homogeneity generally improved, with more consistent nanorod structures being observed. However, as mentioned earlier, excessively long synthesis times resulted in a decline in quality, with nanorods becoming too long and sometimes starting to aggregate, particularly on glass substrates. On Si substrates, while the effect was less pronounced, overly long nanorods began to exhibit minor irregularities in their structure, potentially due to limitations in the diffusion of reactants as the growth continued.

10. Data Interpretation

To obtain images of the ZnO nanorods, a SEM was employed to analyse the surface morphology, uniformity and structural integrity of the nanorods synthesised on different substrates. The following section provides a comprehensive account of the methodology employed.

Prior to commencing the SEM analysis, it was imperative to ensure that the samples had been meticulously cleaned to remove any contaminants that might impede the imaging process. This stage of the process entailed rinsing the samples with deionized water and subsequently drying them with nitrogen gas. Following the cleaning process, the substrates with the synthesised ZnO nanorods were mounted onto aluminium stubs with the aid of conductive carbon tape. The use of this tape provided a stable base and ensured good electrical conductivity between the sample and the SEM stage, which is crucial for preventing charging effects during imaging. Prior to imaging, the SEM was calibrated to ensure optimal performance. This entailed adjusting the relevant parameters, including the working distance, accelerating voltage, and beam alignment, with the objective of achieving optimal resolution and image contrast.

The appropriate accelerating voltage was selected, typically within the range of 5-15 kV, depending on the material and desired resolution. Lower voltages were employed to mitigate charging effects and minimise beam damage to the nanorods, whereas higher voltages facilitated enhanced penetration and improved resolution for thicker samples. SEM images were captured of different regions across each substrate in order to assess the uniformity and consistency of the nanorod growth. This entailed a systematic scanning of the sample, with images being captured at various locations to obtain a comprehensive view of the nanostructures.

The working distance was set in order to optimise the depth of field and resolution. A shorter working distance was employed for the purpose of higher magnification imaging, with the objective of capturing the fine details of the nanorods.

Images of the nanorods were captured at varying magnifications to facilitate the examination of the structures at different scales. Low magnification provided an

overview of the overall distribution and uniformity, while higher magnification allowed for the examination of individual nanorods for detailed morphological analysis.

To conduct a detailed analysis, high-resolution images were captured at higher magnifications, with a focus on specific nanorods or clusters to study their morphology, surface texture, and any defects or irregularities present. Following the acquisition of the images, a comprehensive analysis was conducted to compare the ZnO nanorods grown on different substrates. This entailed measuring the dimensions of the nanorods, assessing their alignment and distribution, and identifying any structural defects or anomalies.

10.1 Analysis of SEM Images

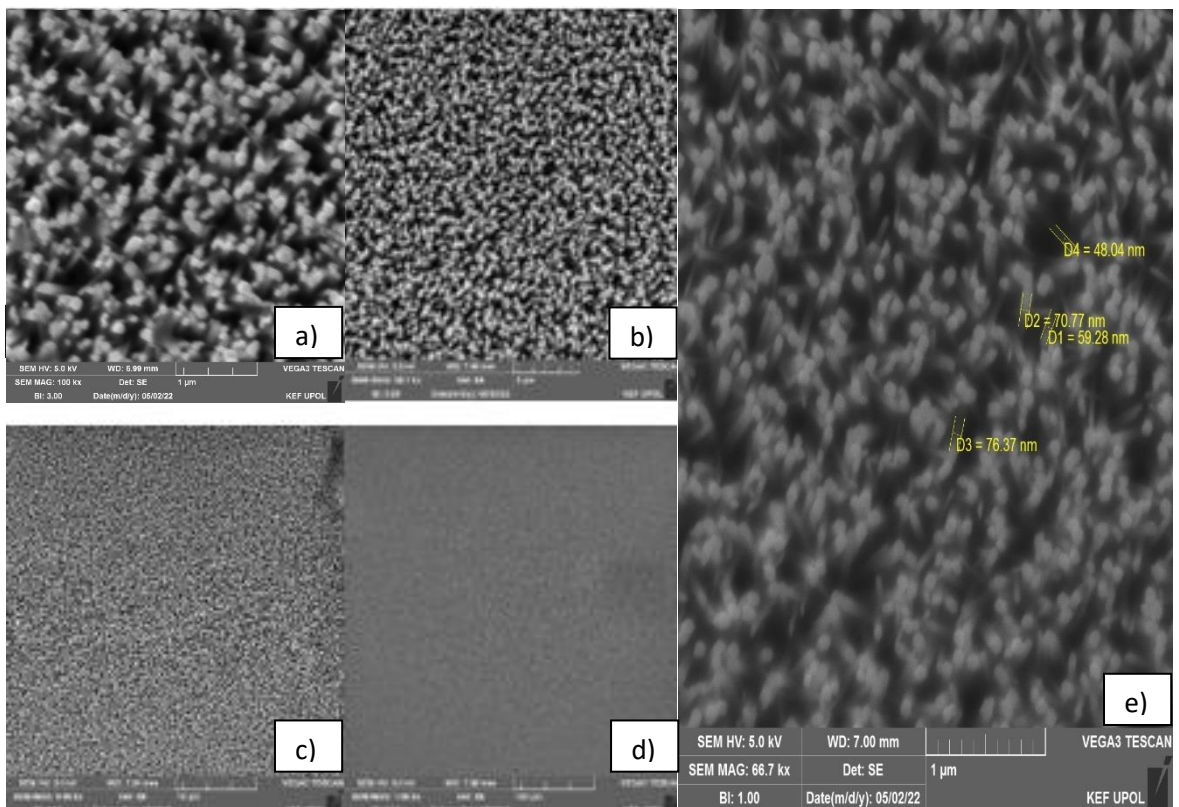


Figure 5. Silicon substrate with ZnO seed layer, captured at various magnifications a) 100 000, b) 40 000, c) 10 000 and d) 1000 to its actual size, e) measurement of the nanorods.

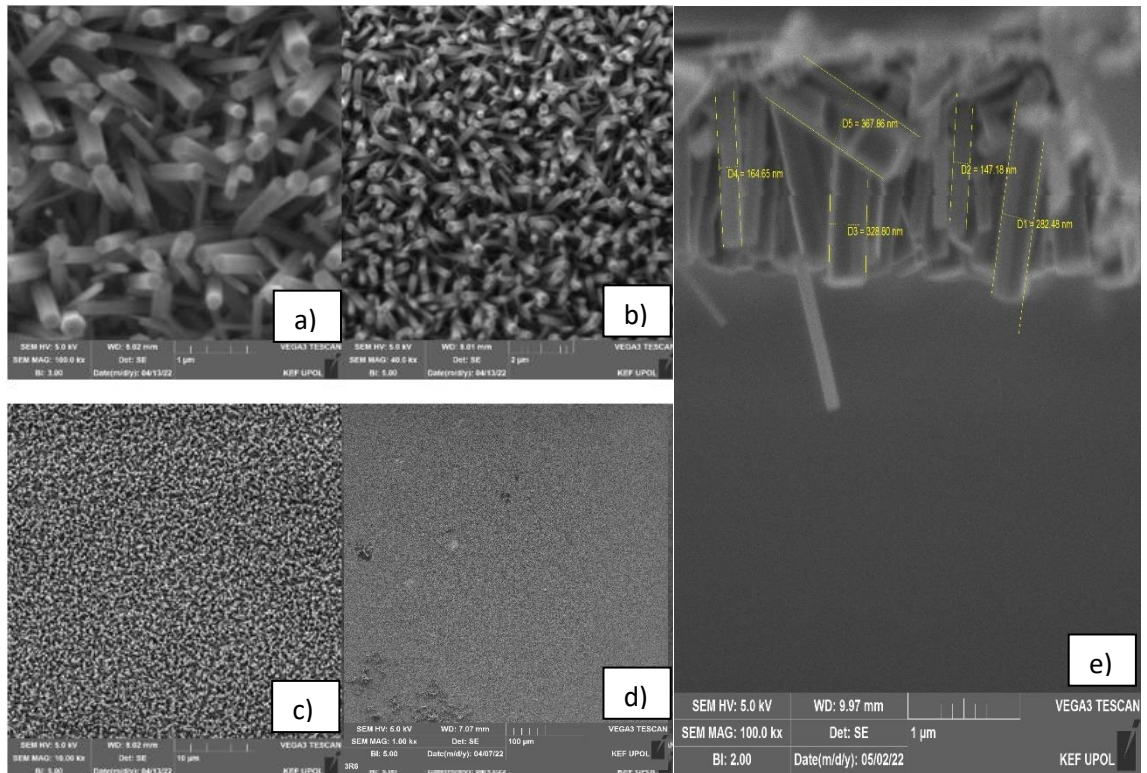


Figure 6: Glass substrate with ZnO seed layer, captured at various magnifications: a) 100 000, b) 40 000, c) 10 000 and d) 1000 to its actual size, e) measurement of the nanorods.

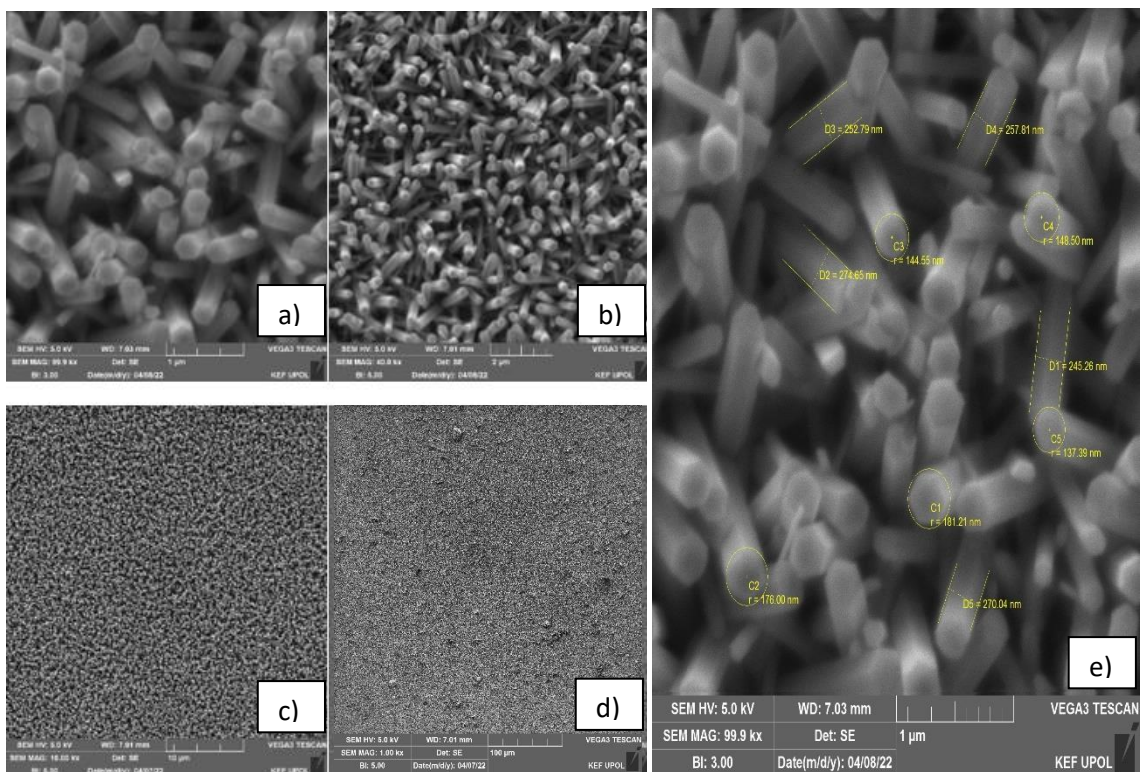


Figure 7: Annealed silicon substrate, captured at various magnifications: a) 100 000, b) 40 000, c) 10 000 and d) 1000 to its actual size, e) measurement of the nanorods.

In order to evaluate the impact of different substrates on ZnO nanorod growth, a detailed analysis was conducted on a number of key characteristics, including morphology, uniformity, and structural integrity. The SEM images provide insights into the influence of each substrate on the formation of the nanorods and their overall quality.

As illustrated in Figure 5, the presence of ZnO nanorods on the Si substrate coated with a thin ZnO layer is clearly visible. The ZnO nanorods grown on the Si substrate exhibit a diameter range of approximately 40 to 80 nm and length range 1 500 to 2 000 nm. The morphology of the rods is well-defined, exhibiting a hexagonal structure with smooth surfaces and sharp edges. The rods are aligned vertically, with minimal aggregation, indicating that the growth process is controlled and orderly, driven by the crystalline nature of the silicon substrate. The nanorods on the silicon substrate exhibit high uniformity in both length and diameter, which is essential for applications that require precise nanostructures. The uniform growth across the substrate indicates that the reaction conditions were optimised for silicon, resulting in a homogeneous array of nanorods.

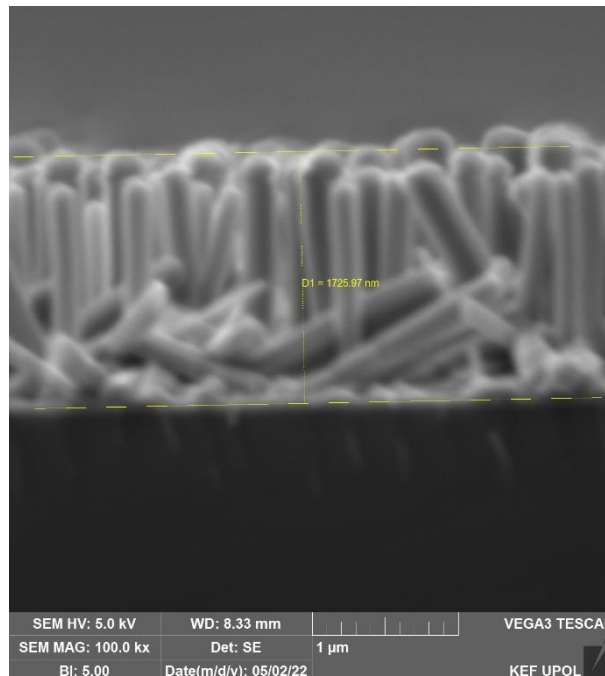


Figure 8: Measurement of ZnO nanorods on a silicon substrate.

The nanorods on the silicon substrate display excellent structural integrity, exhibiting sharp edges and a low incidence of defects. The robust adhesion to the substrate

mitigates the risk of detachment during handling or subsequent processing. The surface coverage on the silicon substrate is dense and consistent, with minimal gaps between the nanorods, indicating efficient nucleation and growth processes. The ZnO nanorods on the Si substrate display high crystallinity, exhibiting well-defined shapes and uniform growth. The crystalline nature of silicon is likely to provide a favourable lattice match for zinc oxide, thereby promoting high-quality nanorod growth [44].

Figure 6 illustrates the morphology of the ZnO nanorods grown on a glass substrate. These nanorods are observed to be longer, ranging from 1,800 to 2,500 nm in length with diameters between 150 and 350 nm. However, the morphology of the rods on the glass substrate displays greater variability compared to those on the silicon substrate. As shown in Figure 8, the rods exhibit a lack of uniformity in shape, including bending, height variation, merging, and irregular growth directions. This inconsistency is likely due to the amorphous nature of the glass substrate, which lacks the crystalline guidance needed for orderly growth. Notably, the nanorods on the glass substrate, including those on the annealed variant, exhibit similar structural irregularities, such as bending and anomalous growth. The weaker adhesion to the glass may contribute to these defects, potentially leading to detachment or mechanical damage during further processing. Additionally, the nanorods on the glass substrate are distributed more sparsely, with visible gaps, likely due to lower nucleation efficiency and reduced adhesion strength. The reduced crystallinity and structural imperfections of the nanorods on the glass substrate can be attributed to the amorphous nature of the glass, which exacerbates crystalline defects [45].

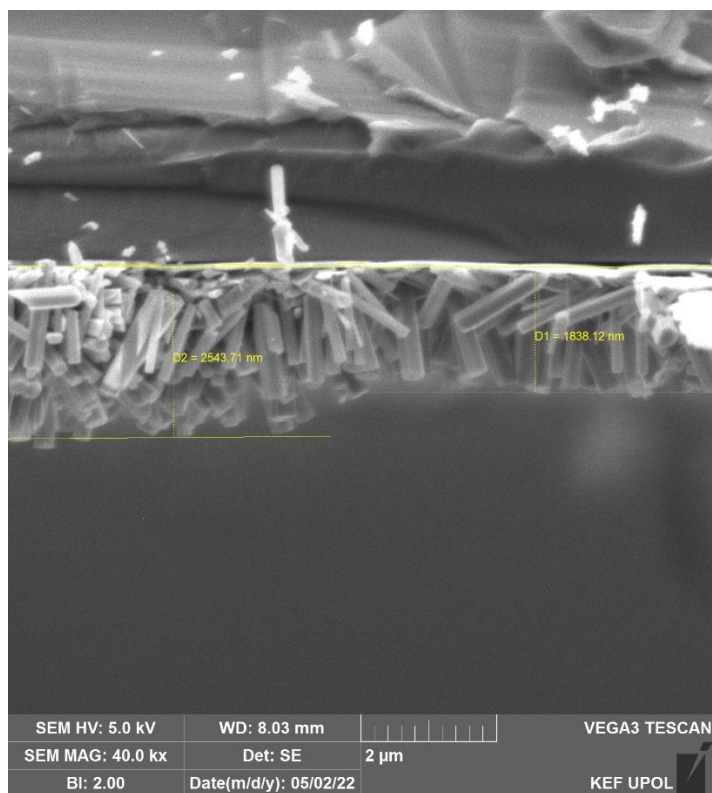


Figure 9: Measurement of ZnO nanorods on a glass substrate.

Figure 7 illustrates the annealed silicon substrate. The annealed SI substrate results in the formation of nanorods with lengths about 2 000 nm and diameter between 150 and 300 nm. As observed with those on the glass substrate, these rods display greater morphological variability. Some rods retain a hexagonal shape, whereas others display evidence of deformation, such as merging at the tips or irregular growth patterns. This indicates that the annealing process may have induced stress, resulting in a modification of the crystal structure and a reduction in the control of the growth process. As with the glass substrate, the annealed silicon substrate displays a lesser degree of uniformity in comparison to the silicon substrate. The variations in size and orientation of the rods are more pronounced.

Annealing can cause stress and alter growth dynamics, leading to inconsistencies. The structural integrity of the nanorods on the annealed substrate is somewhat compromised. It is observed that bending or merging occurs in some rods, which may be attributed to thermal stress during annealing. This could result in a reduction in mechanical stability and an increase in susceptibility to damage [60].

As with the glass substrate, the annealed silicon substrate displays a lower surface coverage than silicon, with an increased number of gaps between the nanorods. This can be attributed to either partial detachment or a less effective nucleation process during synthesis, which may have been influenced by the annealing process [60]. Similar crystallinity issues are observed on the annealed silicon substrate. The thermal treatment may have introduced dislocations or other crystalline imperfections, negatively impacting the nanorods' overall quality.

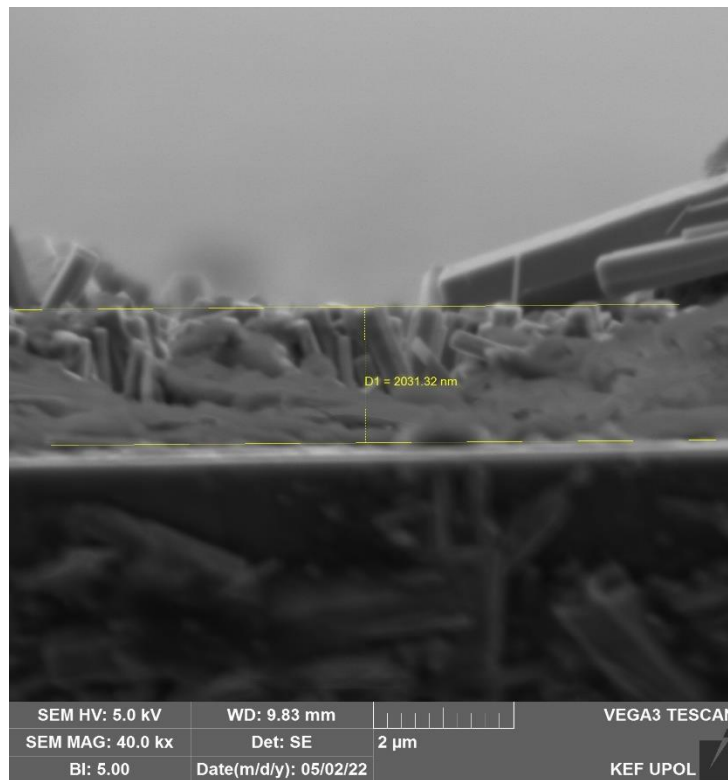


Figure 10: Measurement of ZnO nanorods on an annealed silicon substrate

In conclusion, the Si substrate has been demonstrated to consistently produce nanorods of superior quality. These are characterised by a well-defined hexagonal morphology, high uniformity, and excellent structural integrity. This indicates that the crystalline nature of Si provides an optimal template for the orderly growth of ZnO nanorods, resulting in lengths of approximately 1 700 nm (figure 8). Conversely, the glass and annealed silicon substrates, which yield slightly longer nanorods, demonstrate greater variability and imperfections. Similarly, the annealed silicon substrate displays morphological deformations and reduced uniformity, which are likely due to the stress induced by the annealing process.

11. Conclusion

This bachelor's thesis investigates the growth of zinc oxide nanorods using hydrothermal synthesis, with a particular focus on optimising synthesis parameters and gaining insight into the underlying growth mechanisms. ZnO nanorods. The following are the key findings of the study.

The selection of the substrate was identified as a pivotal factor influencing the quality of the resulting nanorods. The silicon (Si) substrate with thin ZnO layer was found to be the most effective of the four tested substrates in producing ZnO nanorods with superior morphological characteristics. The nanorods that were grown on the silicon substrate exhibited well-defined hexagonal cross-sections, uniform lengths of approximately 1 700 nm and diameters ranging from 40 to 80 nm. Furthermore, the nanorods displayed excellent structural integrity, exhibiting minimal defects and strong adhesion to the substrate, rendering them ideal for applications that require precise and reliable nanostructures.

In contrast, the synthesis of nanorods on the glass substrate with thin ZnO layer demonstrated considerable variability in length (1 800 to 2 500 nm) and morphology. The absence of a crystalline structure in glass resulted in irregular growth patterns, with a considerable number of nanorods displaying bending, merging, or inconsistent diameters. Annealed silicon substrate displays morphological deformations and reduced uniformity.

Temperature is a crucial factor in hydrothermal synthesis, affecting reaction rates, the solubility of reactants, and the diffusion of ions. The impact of varying the synthesis temperature from 85°C to 95°C was investigated. A temperature of 85°C, though previously hypothesised to improve uniformity by slowing growth, proved to be insufficient to significantly enhance the quality of the nanorods. This indicates that the temperature does not provide adequate thermal energy for optimal nanostructure formation. Conversely, an increase in temperature to 95°C resulted in accelerated growth but also introduced greater variability in nanorod dimensions. This is likely due to the heightened nucleation rates and reactant solubility fluctuations that occur at higher temperatures. These findings emphasise the importance of carefully controlling

the temperature to achieve effective growth and a high-quality nanorod morphology. The experiments indicate that 90°C represents an optimal synthesis temperature, offering a compromise between growth rate and structural uniformity, and thus represents an ideal temperature for the production of well-defined ZnO nanorods on Si substrates.

The duration of the hydrothermal process has a direct impact on the growth of ZnO nanorods. Shorter synthesis times typically resulted in incomplete growth, with the nanorods exhibiting reduced length and weaker adhesion to the substrate. For instance, in the case of glass substrates, shorter durations resulted in the formation of non-uniform nanorods with poor structural integrity. Conversely, an extension of the synthesis time beyond the optimal range resulted in overgrowth, whereby the nanorods became excessively long and prone to structural instability.

The frequency of stirring during synthesis was observed to have a minimal impact on the overall quality of ZnO nanorods within certain ranges. However, it was observed that inconsistent stirring could result in localised variations in temperature and reactant concentration, which may in turn affect the uniformity of the nanorods. It is therefore recommended that a consistent and optimal stirring rate be maintained in order to ensure homogeneous growth conditions throughout the synthesis process.

It is recommended that the following areas be the subject of further investigation in future work. While this thesis has provided valuable insights into the hydrothermal synthesis of ZnO nanorods, several areas for further improvement and exploration have been identified.

Further studies should investigate the use of alternative substrate materials and surface treatments to enhance the quality and uniformity of ZnO nanorods. For instance, modification of the surface roughness of the substrate could enhance the adhesion and crystalline alignment of the nanorods.

Temperature control is a crucial aspect of the synthesis process. Improved temperature control during the synthesis process may result in more consistent outcomes. The implementation of more precise temperature monitoring and regulation techniques,

such as the utilisation of a thermostated bath or advanced heating systems, could serve to minimise temperature fluctuations and thereby enhance the reproducibility of the synthesis process.

Adjustments to the synthesis time may be required. A systematic variation of the synthesis duration in increasingly small increments may assist in identifying the optimal time for achieving an optimal balance between nanorod length, uniformity, and structural integrity. Furthermore, an investigation into the impact of intermittent versus continuous synthesis could offer insights into the dynamics of nanorod growth.

In conclusion, the hydrothermal synthesis of ZnO nanorods is a complex process, the outcome of which is influenced by a number of factors, including the choice of substrate, temperature, duration of synthesis and stirring conditions. This thesis has demonstrated that optimising the aforementioned parameters is crucial for achieving high-quality ZnO nanorods with the desired morphological and structural properties. The findings emphasise the significance of substrate crystallinity, meticulous temperature regulation and harmonious synthesis durations in the generation of uniform and well-defined nanorods.

List of Symbols and Abbreviations

ZnO	zinc oxide
PL	photoluminescence
CL	cathodoluminescence
UV	ultraviolet
LED	light Emitting Diode
CBD	chemical Bath Deposition
PLD	pulsed Laser Deposition
HMTA	hexamethylenetetramine
Si	silicon
$C_6H_{12}N_4$	hexamethylenetetramine
HCHO	formaldehyde
NH_3	ammonia
$Zn(OH)_2$	zinc hydroxide
$Zn(NO_3)_2$	zinc nitrate
NaOH	sodium hydroxide

Bibliography

1. Umar, A., C. Ribeiro, and A. Al-Hajry, Growth of Highly c-Axis-Oriented ZnO Nanorods on ZnO/Glass Substrate: Growth Mechanism, Structural, and Optical Properties. *Journal of Physical Chemistry C*, 2009. **113**: p. 14715 - 14720.
2. Wang, X., & Li, Y. Surfactant-Assisted in situ Chemical Etching of ZnO Nanowires. *Journal of Physical Chemistry C*, 2009, **113**(1), p: 41-47.
3. Huang, M.H., S. Mao, and H. Feick, *Room-temperature ultraviolet nanowire nanolasers*. Science, 2001. **292**: p. 1897.
4. Li, C., Y. Zhang, and M. Mann, Stable, selfballasting field emission from zinc oxide nanowires grown on an array of vertically aligned carbon nanofibers. *Applied Physics Letters*, 2010. **96**: p. 14311.
5. Santra, S., P.K. Guha, and S.Z. Ali, ZnO nanowires grown on SOI CMOS substrate for ethanol sensing. *Sensors and Actuators B: Chemical*, 2010. **146**: p. 559.
6. Li, F.M., S. Dalal, and M.C. Newton, Zinc oxide nanostructures and high electron mobility nanocomposite thin film transistors. *IEEE Transactions on Electron Devices*, 2008. **55**: p. 3001.
7. Law, M., L.E. Greene, and J.C. Johnson, Nanowire dye-sensitized solar cells. *Nature Materials*, 2005. **4**: p. 455.
8. Wang Z. L. and S. J., Piezoelectric nanogenerators based on zinc oxide nanowire arrays. *Science*, 2006, **312**.
9. M. Jeong, B. Oh, and M. Ham, Electroluminescence from ZnO nanowires in n-ZnO film/ZnO nanowire array/p-GaN film heterojunction light-emitting diodes. *Applied Physics Letters*, 2006. **88**: p. 202105.
10. Akgun, M.C., E.Y. Kalay, and H.E. Unalan, Hydrothermal zinc oxide nanowire growth using zinc acetate dihydrate salt. *Journal of Material*, 2012. **27**: p. 1445-1451.
11. Litton, C.W. & Reynolds, D.C., Zinc Oxide Materials for Electronic and Optoelectronic Device Applications, 2011, **10**. 1002/9781119991038.
12. Segets, D.; Gradl, J.; Taylor, R.K.; Vassilev, V.; Peukert, W. Analysis of optical absorbance spectra for the determination of ZnO nanoparticle size distribution, solubility, and surface energy. *ACS Nano*, 2009, **3**, p. 1703–1710.
13. Bacaksiz, E.; Parlak, M.; Tomakin, M.; Özcelik, A.; Karakiz, M.; Altunbas, M. The effect of zinc nitrate, zinc acetate and zinc chloride precursors on investigation of structural and optical properties of ZnO thin films. *J. Alloy. Compd* 2008, **466**, p. 447–450.
14. Wang, Z.L. Splendid one-dimensional nanostructures of zinc oxide: A new nanomaterial family for nanotechnology. *ACS Nano* 2008, **2**, p. 1987–1992.

15. Ludi, B.; Niederberger, M. Zinc oxide nanoparticles: Chemical mechanism and classical and non-classical crystallization. *Dalton Trans* 2013, **42**, p. 12554–12568.
16. Yao, B.D., Y.F. Chan, and N. Wang, *Formation of ZnO nanostructures by a simple way of thermal evaporation*. *Applied Physics Letters*, 2002. **81**.
17. Wang, Y.-C., Liu, I.-C., & Huang, M.-H. Fabrication and Optical Properties of Large-Scale Uniform Zinc Oxide Nanowire Arrays by One-Step Electrochemical Deposition Technique. *Journal of Materials Chemistry*, 2002, **12**(11), p: 3287-3292.
18. Lorenz M., J. Lenzner, and E.M. Kaidashev, *Cathodoluminescence of selected single ZnO nanowires on sapphire*. *Ann. Phys-Berlin*, 2004. **13**.
19. Sun, L., Ye, Z. F., Ma, L. A., & Zhang, Y. A. *Improving field emission performance of patterned ZnO electron emission source by optimizing array spacing*. *Vacuum*, 2022.
20. Wang, Z. L. Zinc oxide nanostructures: Growth, properties and applications. *Journal of Physics: Condensed Matter*, 2004, **16**.
21. Laila, I. K. R., Mufti, N., Maryam, S., Fuad, A., Taufiq, A., & Sunaryono. Synthesis and characterization of ZnO nanorods by hydrothermal methods and its application on perovskite solar cells. *Journal of Physics. Conference Series*, 2018, **1040**.
22. Fan, Z., & Lu, J.G. Zinc oxide nanostructures: Synthesis and properties. *Journal of Nanoscience and Nanotechnology*, 2005, **5**(10), p: 1561-1573.
23. Chen, W.J.; Liu, W.L.; Hsieh, S.H.; Tsai, T.K. Preparation of nanosized ZnO using α brass. *Appl. Surf. Sci*, 2007, **253**, p. 6749–6753.
24. Xie, Q.; Dai, Z.; Liang, J.; Xu, L.; Yu, W.; Qian, Y. Synthesis of ZnO three-dimensional architectures and their optical properties. *Solid State Commun*, 2005, **136**, p. 304–307.
25. Bitenc, M.; Orel, Z.C. Synthesis and characterization of crystalline hexagonal bipods of zinc oxide. *Mater. Res. Bull*, 2009, **44**, p. 381–387.
26. Zhang, Y., Ram, M. K., Stefanakos, E. K., & Goswami, D. Y. Synthesis, characterization, and applications of ZnO nanowires. *Journal of Nanomaterials*, 2012, 624520.
27. Baruah, S., & Dutta, J. Hydrothermal growth of ZnO nanostructures. *Science and Technology of Advanced Materials*, 2009, **10**, 013001.
28. Htwe, S. Electrical properties of ZnO nanoparticles. *International Journal of Scientific Research in Science, Engineering and Technology*, 2020, **6**(4)

29. Kaur, G., Sharma, A. K., Jassal, M., & Agrawal, A. K. ZnO-poly(acrylonitrile) composite films with improved piezoelectric properties for energy harvesting and sensing applications. *Composites Science and Technology*. 2023.
30. Yi, G.-C., Wang, C., Park, W. ZnO nanorods: Synthesis, characterization, and applications. *Semiconductor Science and Technology*, 2005, **20**(6), p: 567-573.
31. Sun, Y., Zhang, W., Li, Q., Liu, H., & Wang, X. Preparations and applications of zinc oxide based photocatalytic materials. *Advanced Sensor and Energy Materials*, 2023, **2**.
32. Jha, S., Rani, R., & Singh, S. Biogenic zinc oxide nanoparticles and their biomedical applications: A review. *Journal of Inorganic and Organometallic Polymers and Materials*, 2023, **33**, 1437–1452.
33. Mirzaei, H., & Darroudi, M. Zinc oxide nanoparticles: Biological synthesis and biomedical applications. *Ceramics International*, 2017, **43**, 907–914.
34. Bourfaa, F., Boutelala, A., Aida, M. S., Attaf, N., & Ocak, Y. S. Influence of seed layer surface position on morphology and photocatalysis efficiency of ZnO nanorods and nanoflowers. *Journal of Nanomaterials*, 2020.
35. Willander, M., et al. Zinc oxide nanorod based photonic devices: recent progress in growth, light-emitting diodes, and lasers. *Nanotechnology*, 2009, **20**(33).
36. Mayasari, R., Mulyono A., Masmui M. Growth of ZnO nanorods on different substrates using hydrothermal method. *Malaysian Journal of Fundamental and Applied Sciences*, 2020, **16**.
37. Abdallah, B., Zetoun, W., & Tello, A. Deposition of ZnO thin films with different powers using RF magnetron sputtering method: Structural, electrical and optical study. *Heliyon*, 2024, **10**.
38. Gao, W., & Li, Z. ZnO thin films produced by magnetron sputtering. *Ceramics International*, 2004, **30**.
39. Ondo-Ndong, R., Ferblantier, G., Al Kalfioui, M., Boyer, A., & Foucaran, A. Properties of RF magnetron sputtered zinc oxide thin films. *Journal of Crystal Growth*, 2003, **255**.
40. Hasnidawani, J. N., Azlina, H. N., Norita, H., Bonnia, N. N., Ratim, S., & Ali, E. S. Synthesis of ZnO nanostructures using sol-gel method. *Procedia Chemistry*, 2016, **19**, p. 211–216.

41. Yildizay, H. Synthesis and characterization of Ni-doped ZnO thin films prepared by chemical bath deposition. *Ceramics - Silikaty*, 2023, **67**(3), p: 193-199.
42. Sakano, T., Nishimura, R., Fukuoka, H., Yata, Y., Saiki, T., & Obara, M. Pulsed-laser deposition of ZnO thin films and nanorods for photonic devices. *Proceedings of SPIE - The International Society for Optical Engineering*, 2008, **7031**.
43. Ivanova, A. K., Kudryashov, S. I., Minh, P. H., Ionin, A. A., Mel'nik, N. N., & Rudenko, A. A. High-temperature annealing effect on photoluminescence of ZnO nanoparticles produced by laser ablation in hydrogen peroxide. *Journal of Physics. Conference Series*, 2020, **1692**.
44. Al-She'irey, A. Y., Balouch, A., Mawarnis, E. R., Roza, L., Rahman, M. Y. A., Abdullah, & Mahar, A. M. (2022). Effect of ZnO seed layer annealing temperature on the growth of ZnO nanorods and its catalytic application. *Optical Materials*, 2022, **131**.
45. Ali, S. B., Fakhri, M. A., & Gopinath, S. C. B. Effect of annealing process on the physical properties of ZnO nanorods and their performances as photodetectors. *Journal of Optics*, 2024, **53**.
46. Khayatian, A. & Almasi kashi, M. & Azimirad, R. Effect of annealing process in tuning of defects in ZnO nanorods and their application in UV photodetectors. *Optik - International Journal for Light and Electron Optics*, 2016, **127**.
47. Zhang, X., & Li, S. *Hydrothermal synthesis of nanomaterials: A review*. Materials Science and Engineering: R: Reports, 2015, **98**, p. 1-29.
48. Moezzi, A., Cortie, M., McDonagh, A. (2013). Formation of Zinc Hydroxide Nitrate by H⁺-Catalyzed Dissolution-Precipitation. *European Journal of Inorganic Chemistry*, 2013. **10**.
49. Raut, H. K., & Kim, K. H. (2020). *Hydrothermal synthesis of nanomaterials: Mechanisms and applications*. *Journal of Nanoscience and Nanotechnology*, 2020, **20**, p. 7697-7714.
50. Huang, X., & Zhang, J. *Challenges and solutions in hydrothermal synthesis of nanomaterials*. *Advanced Materials Interfaces*, 2019, **6**, 1901265.
51. Brinker, C. J., & Scherer, G. W. The sol-gel process: A comprehensive review of methods and applications. *Journal of Non-Crystalline Solids*, 1990, **120**(1-3).

52. Li, Y., & Wu, M. Comparison of sol-gel and hydrothermal synthesis methods for nanostructured materials. *Journal of Materials Science*, 2007, **42**.
53. Kim, K. H., & Choi, J. S. (2011). Chemical vapor deposition (CVD) of thin films and nanostructures: Principles and applications. *Materials Science and Engineering: R: Reports*, 2011, **72**.
54. Wang, L., & Chen, X. Comparison of precipitation and hydrothermal methods for the synthesis of nanoparticles: A review. *Journal of Nanoscience and Nanotechnology*, 2012, **12**.
55. Zhang, Y., & Wang, Z. L. Electrochemical deposition of nanostructured materials: A review. *Advanced Functional Materials*, 2011, **21**.
56. Goldstein, J. I., et al. (1992). Scanning Electron Microscopy: Principles and Applications. *Scanning Microscopy*, 1992, **6**.
57. Williams, D. B., & Carter, C. B. Introduction to Scanning Electron Microscopy for Materials Characterization. *Materials Characterization*, 2009, **60**.
58. Sharma, K. K., & Singh, S. K. Scanning Electron Microscopy of Nanomaterials: Techniques and Applications. *Journal of Nanoscience and Nanotechnology*, 2013, **13**.
59. Azharuddin, M., Tavares, A. C., & Mendonça, C. R. Synthesis and characterization of ZnO nanorods using Zn acetate precursor and hydrothermal method. *Journal of Nanomaterials*, 2018.
60. M. R. R. Rao, K. S. Narayan, & M. K. Sharma, Effect of annealing on the structural and optical properties of ZnO thin films, *Journal of Materials Science: Materials in Electronics*, 2016, **27**.

Appendix






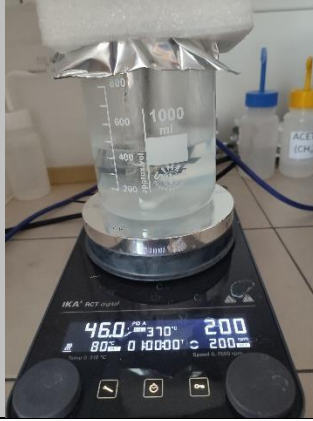

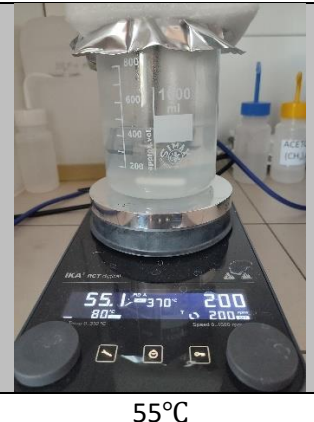

		
20°C	25°C	30°C
		
35°C	40°C	46°C
		
50°C	55°C	60°C

Table 1: *The Effect of Temperature Variation on Solution Transparency (20 °C - 60°C in 5°C Increments).*

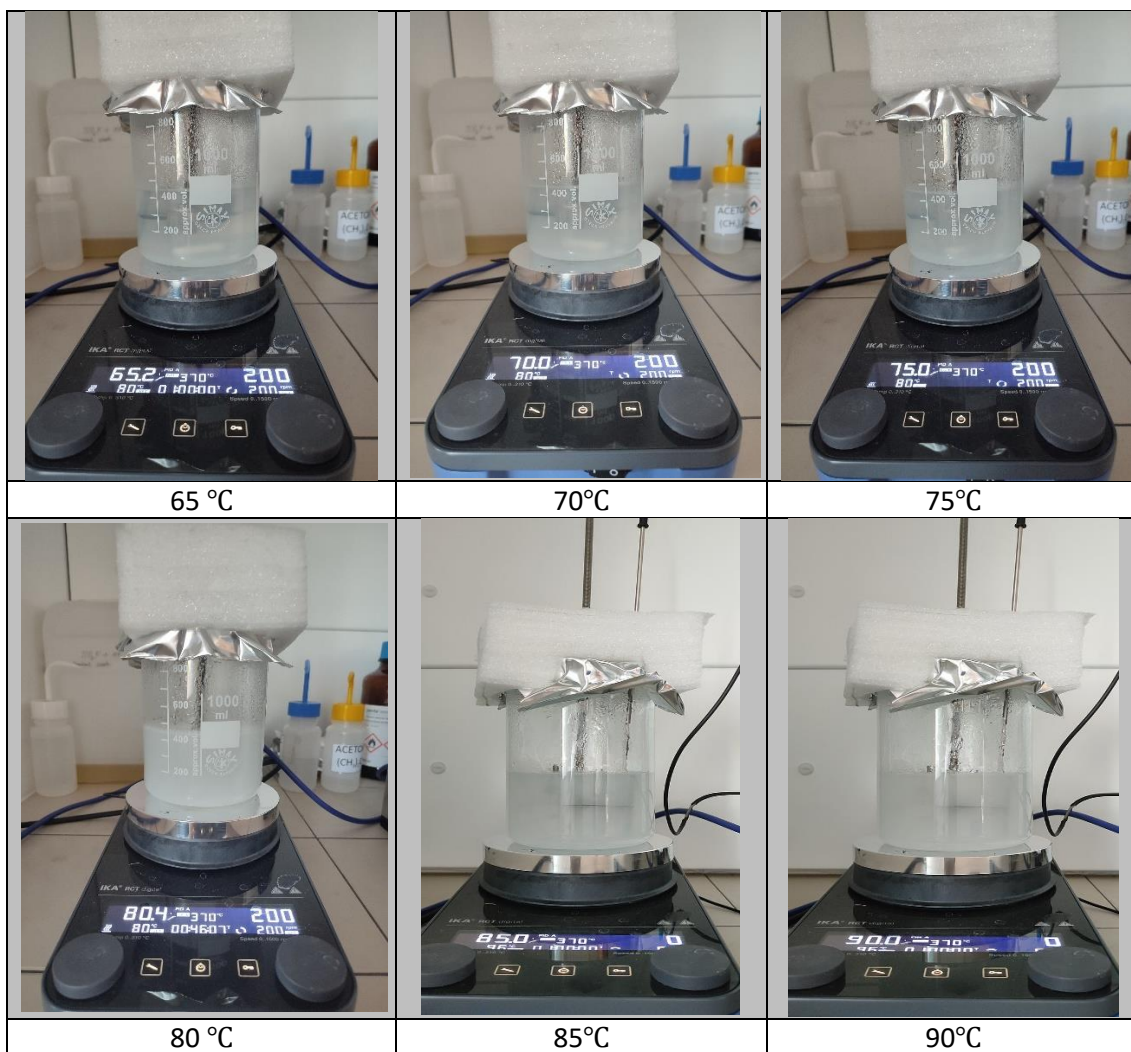


Table 2: *The Effect of Temperature Variation on Solution Transparency (65°C - 90°C in 5°C Increments).*

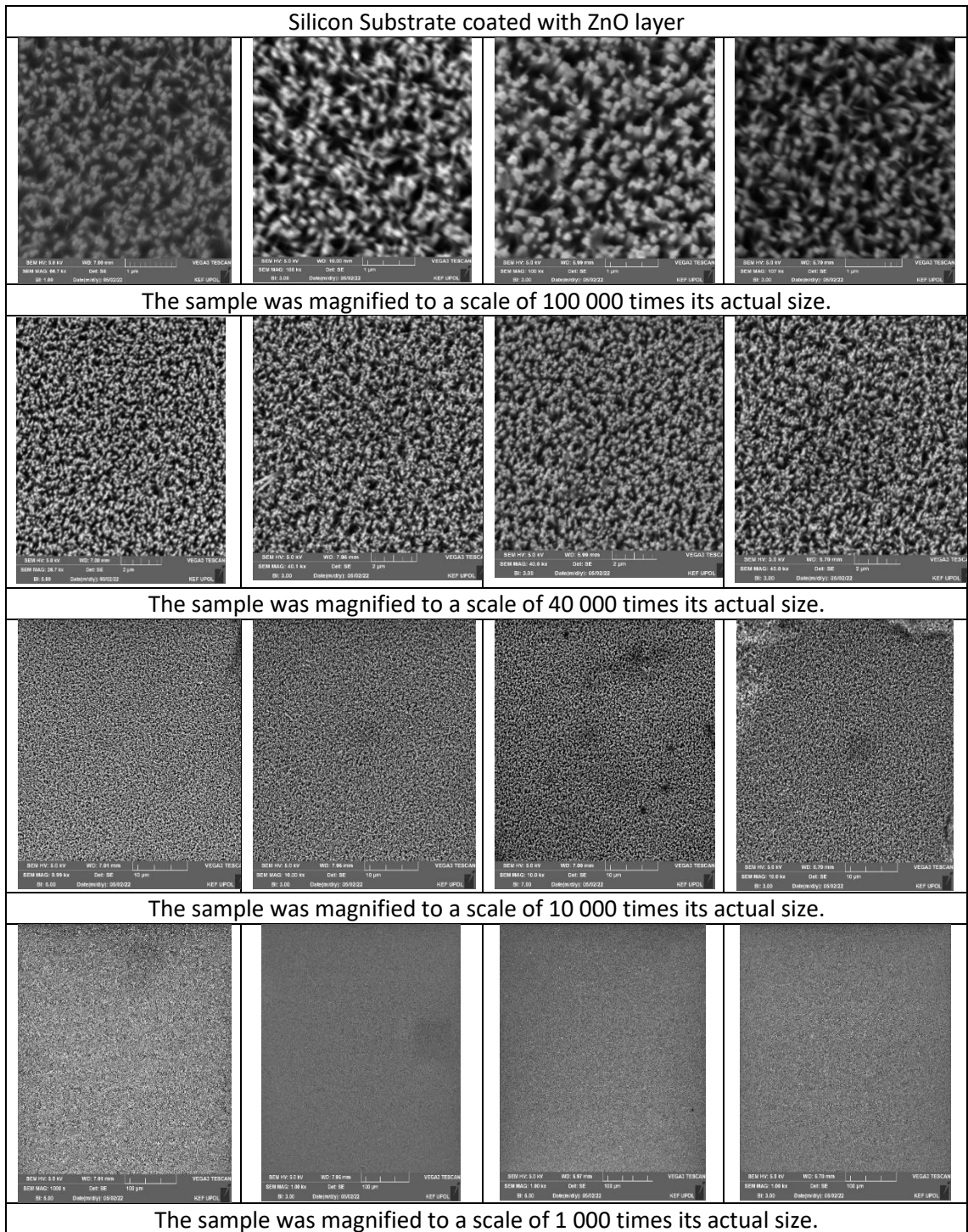


Table 3: ZnO nanorods on silicon substrate coated with ZnO layer displayed at different magnifications.

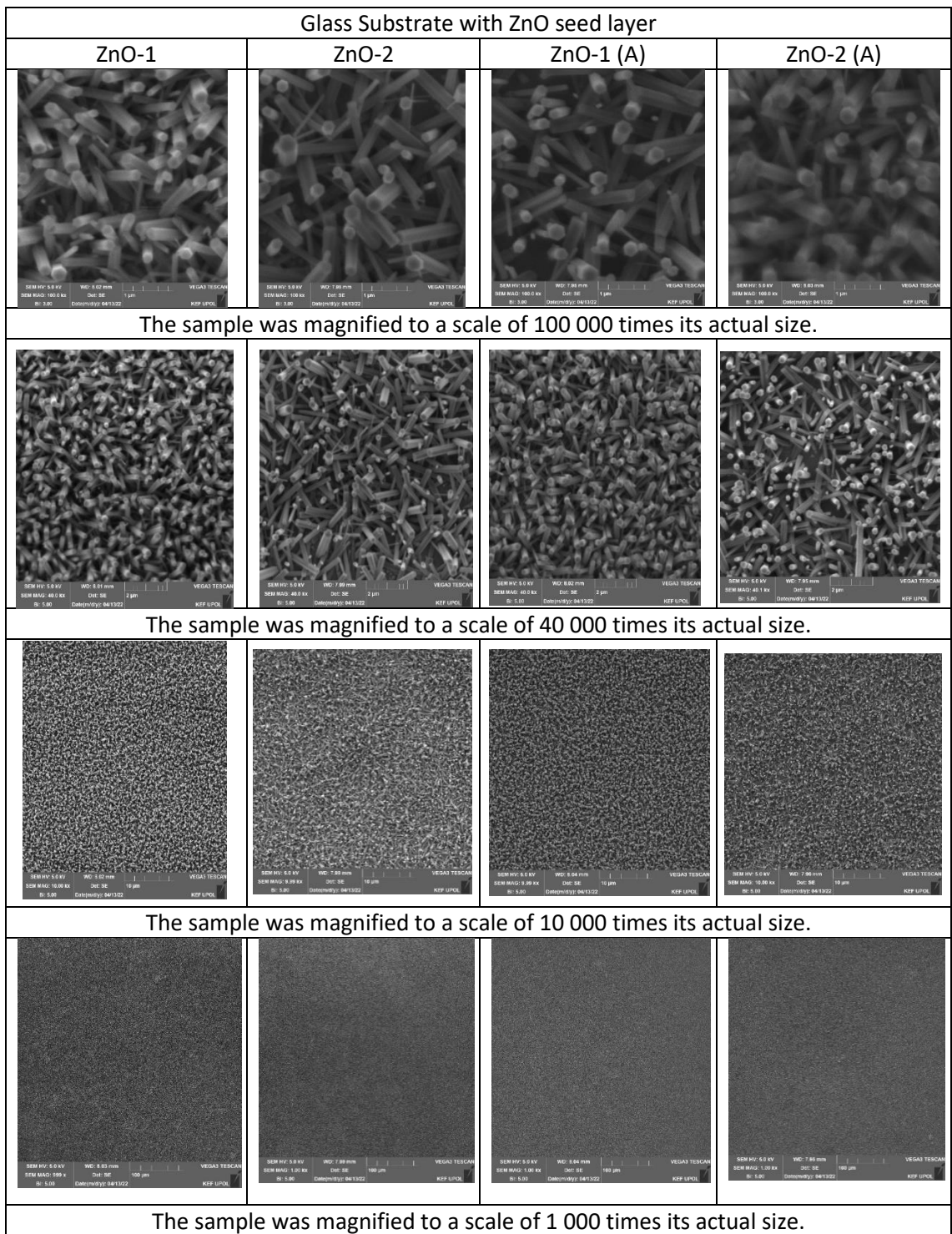


Table 4: ZnO nanorods on glass substrate displayed at different magnifications.

The ZnO nanorods grown on samples ZnO-1 and ZnO-2 showed no visible difference in morphology compared to those on ZnO-1(A) and ZnO-2(A), where ZnO-1(A) and ZnO-2(A) were annealed for 20 minutes at 0.5 Pa and 0.25 Pa

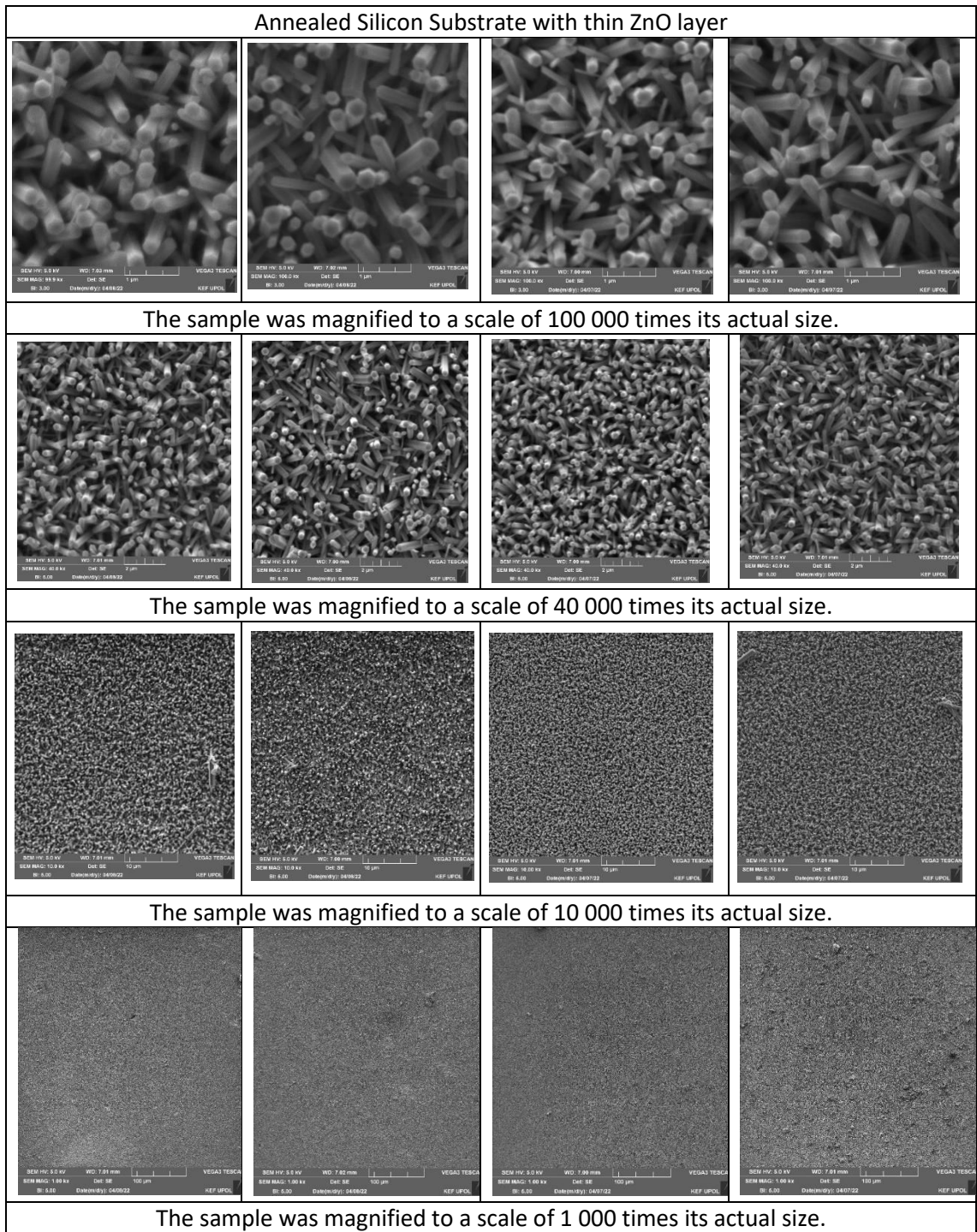


Table 5: ZnO nanorods on annealed silicon substrate displayed at different magnifications.

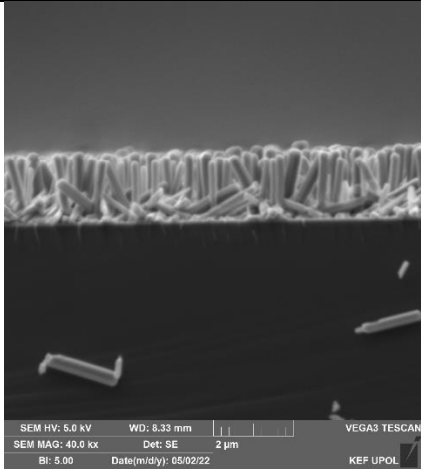
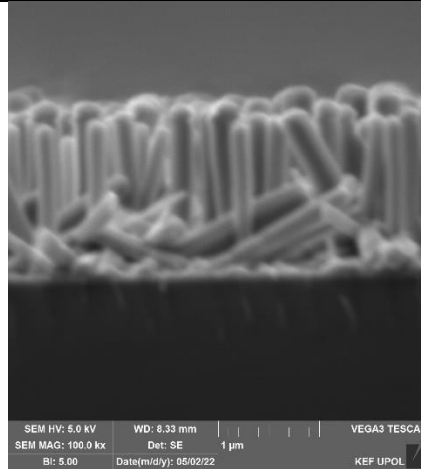
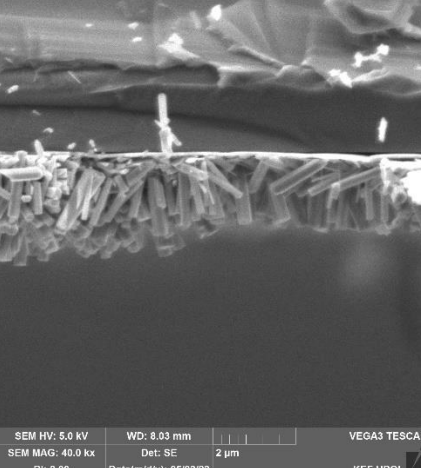
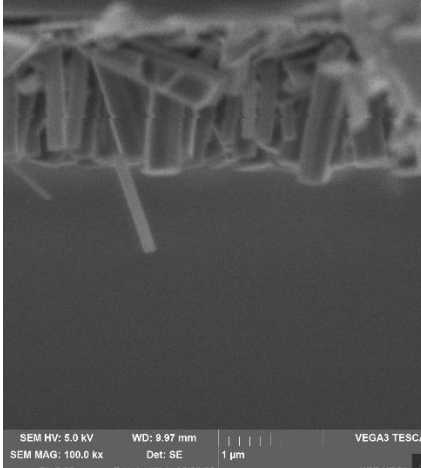
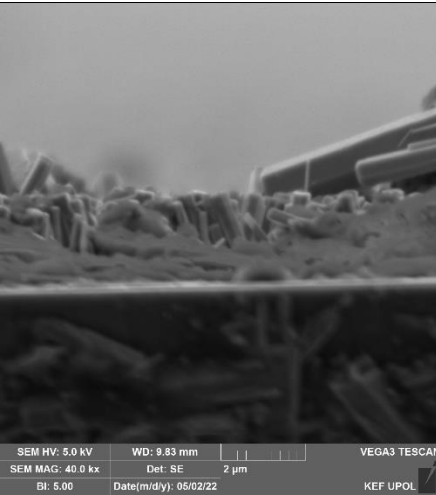
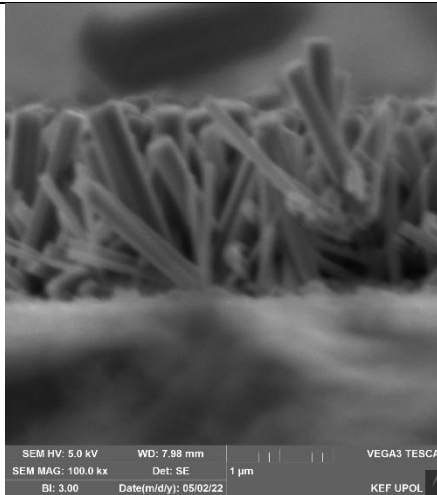
Silicon Substrate	
	
40 kx	100 kx
Glass Substrate	
	
40 kx	100 kx
Annealed Silicon Substrate	
	
40 kx	100 kx

Table 6: Cross-Sections of Silicon, glass and annealed substrates.