## ZNO NANOSTRUCTURE: A REVIEW ON THEIR GROWTH AND STRUCTURAL PROPERTIES BY THERMAL EVAPORATE AND CHEMICAL VAPOR DEPOSITION METHODS

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#### ABSTRACT

In the past several decades, One-dimensional (1D) Zinc Oxide (ZnO) nanostructure was a unique material and ZnO has been extensively and intensively studied. Also, ZnO shows semiconducting and piezoelectric binary properties. Using of different techniques, nanowires, nanobelts, nanorings and nanosprings of ZnO had been fabricated under specific growth conditions. Since, ZnO has a wide band gap (3.37 eV); large exciton binding energy (60 meV) and it could lead to lasing action based on exciton recombination. ZnO is one of the materials that has extraordinary physical and chemical properties, also for current and future it would be different electronic and optoelectronic device applications. This paper reviews the different nanostructures of ZnO grown by two technique, for example, thermal evaporate and chemical vapor deposition also, comparison with together their corresponding growth mechanisms. The application of ZnO nanowire as nano-sensors and field effect transistors is demonstrated.

#### **Keywords:**

Zinc oxide, Nanostructure, Growth ZnO, Thermal Evaporation, Chemical Vapor Deposition

## INTRODUCTION

Zinc oxide (ZnO) is a vital matter for fabrication nanowire's and thin films. Study on the ZnO nanowire started by many researchers from the 1969s, synthesised to nanowires and thin films have been an active field because it has several applications. Also, Zinc oxide is a key of technological material. Nanomaterials of the same zinc oxide has been proven to be a unique functional material during the last several years, which has been extremely used in field emission [1], electro-acoustic transducers [2], short wavelength optoelectronics [3], gas sensors [4], transparent conducting coating materials [5], piezoelectric devices [6], and photo-catalysis [7].

Characterisation of ZnO nanowires has been an active and attractive field reason that their applications as sensors and catalysts for solar cell fabrication. With the reduction in size, we will have novel physical, chemical and optical properties introduced. In addition, ZnO has physical properties include a wide and direct band-gap of 3.37 eV compound semiconductors that are suitable for short wavelength optoelectronic applications and large exciton binding energy for example (60 meV). Also in ZnO nano-crystal can ensure efficient excitonic emission at room temperature (300 K) and ultraviolet (UV) photoluminescence has been reported in disordered nanoparticles and nanowires.

#### ZNO NANOWIRES GROWTH METHOD

There are several methods applied to growth of ZnO nanowires and thin films, for example, thermal evaporation[8], annealing in a reactive atmosphere, molecular beam epitaxy (MBE) [9], laser ablation [10, 11], solution based method [12] and chemical vapor deposition (CVD) [13]. We want to focus on the synthesis of ZnO nanowires from zinc salts in solution. Also, chemical vapor deposition and thermal evaporation are widely used methods of physical vapor deposition (PVD) [14].

In this section, we discuss two methods, such as thermal evaporation and chemical vapor deposition for the growth and morphologies of 1D-ZnO nanostructures. The growth and morphologies of doped and structures of 1D-ZnO nanostructures are reviewed. Nanowires with very long-length can be synthesised this way [15]; so far, the substrates used are the same silicon or zinc and other FTO-coated glasses since that high-CVD growth temperature is one of the easy damages the transparent conducting oxide [16]. Furthermore, since the nanowires are not directly synthesised on FTO-coated substrates, a nanowire transfer stage is needed in the subsequent solar cell fabrication. Such a transfer stage causes contact issues between the nanowires. In spite of, most of the methods are not well suited for in-large area coating, low-temperature processing. However, the above mentioned methods could not be used for ZnO crystal fabrication below 150 °C. Then the equipment is expensive for large area process. In spite of, chemical vapor deposition (CVD) has been an attractive technology which is simple for thin-film to make.

There are several previous papers discussing the ZnO nanowires using electro-less deposition in solution bath and indicating to possible of low temperature [17]. Preparation of nanowire in a chemical solution, bath, presents several advantages: for instance, thin films can be obtained on substrates at low temperature, below 100 °C, also, the thickness and morphology of the film can be controlled via deposition parameters, furthermore the mobilisation is relatively cheap, and in addition, the method is more environmentally friendly.

These supply the technique compatibility for the easy and low-cost process and good quality for nanowire fabrication. In the present paper, we decided the patterning technique of ZnO nanowire and performed the bottom-gate type transparent thin film transistors (TFT) [18] device with a patterned active channel ZnO film on that used CBD method. Also, the properties of films and synthesis of ZnO were studied. This is reported in the summary of the studies on solution growth and the resulting structures. As can be seen in the summary of different work in Table 1.

Table 1: Summary of Various Results and Methods for Aqueous Solution Growth ZnO.

Growh solution	Morphology	Focus of investigation
Zinc nitrate, HMT	Nanotubes	Influence of substrate and
		seed layer [19]
Zinc nitrate,HMT	Micro tubes	On Si and conducting,
		glass substrates [20], [21]
Zinc nitrate, zinc acetate,	Highly. Aligned	Influence of substrate and
HMT	Nano rods	seed layer [22], [23]
Zinc-nitrate, HMT, citrate	Oriented nanocolums	Control of aspect ratio:
		Nano Figures, addition of
		citrate anions decreases
		aspect ratio [24]
Zinc nitrate,	Ordered Nano rods	Influence of substrate and
triethanolamine, HCl (pH		counter ions growth
5)		solution [25]
Comparison of different	Star-like, Nano rods	Influence of reaction
growth solutions		conditions: ligand,
		counter-ions, pH, ionic
		strength, and deposition
		time [19]
Zinc acetate, sodium	Disk-like, flowerlike,	Influence of pH on
hydroxide, citric acid	Nano-rods	growth solution [26]
Zinc nitrate, thiourea	Nanowires, flower-like,	Influence of reactants,
	tube-like	substrate pretreatment
		[27]

Andrés-Vergés et al. have also done studies on ZnO crystal morphology. They looked at experimental conditions for both Zinc chloride/HMTA and Zinc Nitrate/HMTA starting reactants [28]. They were able to determine under which precursor concentrations and reaction temperature produced the needle-like structures and those that produced the prism-like nanostructures.

## THERMAL EVAPORATIONS METHOD

Nowadays, thermal evaporation is one of the most widely used applications of physical vapor deposition (PVD). This way is a kind of thin film deposition, which it is a vacuum mechanism wherein coatings substrate of pure materials is applied over the surface of many different objects. The deposited coatings ordinarily have a thickness in the range of nanometers to microns and are of a mixed single material or layers of multiple materials. Furthermore, For the grow of ZnO by thermal evaporation method two matter are important such as, gases flow rate in a vacuum chamber and annealing temperature. In coming paragraph, both issues will be explained.

First of all, gases flow rate in the chamber is one of the important matters for growing quality of ZnO nanowire. Change of gas in a vacuum chamber used chang of quality of ZnO. For example, Yanjun Fang et al. studied on property and growth of ZnO nanowire arrays by Thermal Evaporation [29]. The growth of well-aligned ZnO nanowire arrays (see Figure 1) was carried out in a horizontal quartz tube inserted into a tube furnace.



Figure 1: SEM figures: (a) the SnO<sub>2</sub> :F surface of the conducting glass substrate, (b) ZnO layer deposited by spray pyrolysis on conducting glass, (c) planar view (45° tilted) and (d) cross section of electrodeposited ZnO(20 c cm<sup>-2</sup>) on a glass /SnO<sub>2</sub>:f / ZnOSP sample [30]

It is interesting to know that the change of oxygen flow rate has a significant impact on the morphology of the as grown products. As can see, when the oxygen flow rate is increasing the mean diameter of the nanowire arrays does not go on to increase. Figure 2 shows this fact.



Figure 2: Evolution of the morphology of the as-grown ZnO nanostructures with the change of the oxygen flow rate (growth time: 60 min): top view SEM images with the oxygen flow rate of (a) 0, (b) 15, (c) 25, (d) 45, and (e) 75 sccm. Corresponding cross-section view SEM images are shown in the insets [29]

The oxygen flow rate and high-purity Ar gas during the growth process plays an essential role in the morphology evolution of the as-grown products, which results in the change from 2D to 1D growth and finally to 2D growth. As secondly approach, one of the another important matter to real growth ZnO nanowire is changing annealing temperature. At the same time D. Calestani did testing about low-temperature thermal deposition for growth of aligned

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ZnO, and he obtained on both doped and undoped ZnO seeding films [17]. The observed nano rods (Figure 3) were usually rather homogeneous in diameter and length that, respectively, vary within 30-50 nm and 0.5-3 mm ranges depending on the growth conditions. Also, no morphological difference has been detected in the nanostructures grown on these two different kinds of film. Also, the test was done in temperatures below 500 °C.



Figure 3: SEM images of the obtained arrays of vertically aligned ZnO nanorods: (a) tilted the view; (b) higher magnification image with the typical size of a nanorod; (c) cross-section view of a fractured zone, where the ZnO film-rod structure is clearly visible. (d) XRD spectra of a seeding ZnO film before and after the growth of ZnO nanorods; preferential orientation along the c-axis of the wurtzite hexagonal structure is clearly visible in both samples. (e) SEM top view image that shows vertical alignment and planar distribution [17]

The coating materials can be either molecule, including nitrides and oxides or purely atomic elements such as both metals and non-metals. The materials used to cover is called the substrate, which can be many different things, including semiconductor wafers, optical components, and solar cells. Thermal evaporation is a mechanism wherein a solid material is heated inside a high-vacuum chamber to a temperature which generates some vapor pressure. Inside the vacuum, even a very low-vapor pressure is adequate to create a vapor cloud within the chamber. This evaporated material now including of a vapor stream, which passes through a vacuum, and sticks onto the substrate as a wire or coating. Since, in the majority of cases, the material becomes liquid by heating it to its melting temperature, it is commonly placed in the bottom of the chamber, often in some form of upright crucible.

The vapor then rises above from this bottom source and reaches the substrates that are held inverted in suitable fixtures at the top of the chamber, with surfaces to be coated facing down toward the rising vapor to acquire their coating. Different measures may have to be taken in order to ensure film adhesion and control various film properties as desired.

CHEMICAL VAPOUR DEPOSITION (CVD) METHOD

One of the methods, for growing zinc oxide (ZnO), is Chemical Vapor Deposition (CVD) method. In this article, reported on the experimental data resulting from several researcher attempts to understand how zinc oxide (ZnO) can be grown on various substrate via a solid-vapor-solid process in an experimental made of chemical vapor deposition (CVD) apparatus using of a solid source. Different growth parameters such as growth temperature and different gas injection rate were used to change the ZnO nucleation process. Deposited thin films were characterised via photo-luminescence and scanning electron microscopy [31]. We found that Means of CVD method could grow ZnO nanowire or thin films with the thin film quality comparable to these grown by the most expensive apparatuses such as metal-organic chemical vapor deposition (MOCVD) [32]. Furthermore, for growth of ZnO nanowire by chemical vapor deposition two factors are very important, for example, synthesis and characterisation.

Firstly, zinc oxide synthesised directly on FTO/ITO-coated glass substrates in a horizontal furnace at a low temperature, where the nanowire growth followed a self-catalytic the same vapor–liquid–solid mechanism [33]. Figure 4 shows schematic of nanowire synthesis [34]. Moreover, quartz tube was mounted on a single-zone furnace that almost constant temperature heating zone of about 13 cm long. Also in Figure 4, a particular designed cylindrical source container with an inner diameter of almost 1.4 cm, outer diameter of 2.0 cm, as the length of 2.5 cm was used in this experiment. The container including 0.3-g zinc powder as the material was placed at the center of the chamber. FTO-coated glass substrate with a size of almost 1.0  $\times$  1.5 cm<sup>2</sup> was first cleaned via acetone and isopropyl alcohol. In addition, substrate covered via a Si<sub>3</sub>N<sub>4</sub> mask with around 0.5  $\times$  0.5 cm<sup>2</sup> opening in the center.



Figure 4: Schematic of the system setup for nanowire synthesis [35]

Synthesis of growth, the ZnO nanowire, is a vital matter, because it is one of the applications for fabrication of solar cell. Also, chemical vapor deposition is an interesting method for fabricate ZnO nanowire. For instance, J. Baxter et al. worked about growth ZnO nanowires on fluorine-doped tin oxide (FTO) substrate [36]. In addition, transparent conducted substrates that were seeded with a thin film of ZnO nanoparticles, as in the work by Greene [37]. ZnO seed nanoparticles with diameters ranging from 5 to 10 nm were synthesised according to the method described by Pacholski [38]. Furthermore in a study by D.I. Suh, a silicon wafer prior to the ZnO nanowire growth, the samples were cleaned by acetone/isopropyl alcohol sonication and then coated with a layer of Au thin film (2 nm) using an electron-beam evaporation [15]. Following this coating, zinc acetate dehydrate (99.999%, Aldrich Company) was also coated on the substrate, by prior to the ZnO nanowire growth, the samples were cleaned by acetone/isopropyl alcohol sonication and then coated with a layer of Au thin film (2 nm) using an electron-beam evaporation [15]. Following this coating, zinc acetate dehydrate (99.999%, Aldrich Company) was also coated on the substrate, by prior to the ZnO nanowire growth, the samples were cleaned by acetone/isopropyl alcohol sonication and then coated with a layer of Au thin film (2 nm) using an electron-beam evaporation. Following this coating, zinc acetate dehydrate

(99.999%, Aldrich Company) was also coated on the substrate, by dip coating several times in a concentrated ethanol suspension. The additional coating of zinc acetate dehydrate on the both the Si and FTO glass substrates was used as seed nanoparticles for the vertical and branched structures of ZnO nanowire growth. Dip coating several times in a concentrated ethanol suspension. The additional coating of zinc acetate dehydrate on the both the Si and FTO glass substrates was used as seed nanoparticles for the vertical and branched structures of ZnO nanowire growth.



Figure 5: (a) A field-emission scanning electron microscopy (FE-SEM) image of zinc acetate dehydrates seeds coated on the Si substrate. The coated substrate was dried at 350 °C for 20 min. Schematic diagrams (3D and top-view) of the fabrication processes (Step (b–d)) for the branched structures of the ZnO nanowires dye-sensitized solar cells (DSSCs) on the fluorine-doped SnO (FTO) glass substrates. (b) Vertical growth of the ZnO nanowires on the substrates. (c) The coating of the zinc acetate dehydrate Nanoparticles (seeds) on the substrates containing the vertically or randomly grown ZnO nanowires [15]

Secondly, one of the most important sections in growth of the zinc oxide is characterisation and it plays an important role for its use. Zinc oxide has several applications which one of the important applications that is to making solar cells. We review examples of zinc oxide to find a rule for full and comprehensive access. Such as Pai-Chun Chang et al. reported after synthesis, material characterisations, including electrical transport and electron microscopy measurements were performed [39]. The objective was to distinguish the carrier concentration difference and morphology change between the nanowires grown.

#### **RESULTS AND DISCUSSIONS**

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One of the simplest way for fabrication ZnO nanowire is thermal evaporation that depositing material onto a substrate. Also, one major disadvantage of this method is that a lot of material is lost in the process. Purity of the thin film depends on the purity and quality of the source material and the thickness of the films vary according to the geometry of the vacuum chamber. In addition, another simple and cheap way for growth of nanowire is chemical vapor deposition. In the Table 2 using of materials, advantages and disadvantages of two different methods fabricated nanowire compared to each other.

Method	Materials	Advantages	Disadvantages
Thermal	Aluminum,	Simple and	Low melting
evaporate	chromium,	cheap.	point metals.
	copper, gold,	Less substrate	Density and
	nickel,	surface	Adhesion are
	cadmium,	damage.	poor.
	palladium,	Excellent	It is not
	titanium,	purity of	possible to
	molybdenum	films	evaporate the
	, tungsten		Di-electric
	and tantalum		materials. Lost
			of material.
CVD	Alloys,	Produce	Toxic,
	nitrides,	extremely	corrosive,
	oxides, nano-	dense, films	flammable,
	composites,	are highly	low pressure or
	semiconduct	uniform,	ultrahigh
	ors and	processing is	vacuum
	intermetallic	at low	
	compounds	temperatures	

# Table 2: Table for Comparison of Two Methods Thermal Evaporate and Chemical Vapor Deposition.

# CONCLUSION

In the present review article, described two methods, thermal evaporation (physical) and chemical vapor deposition (chemical) for thin films fabrication. It is clear that, thermal evaporation method is one of the oldest methods, but second method is simple, inexpensive, and suitable for large area deposition for good quality thin films. The data presented in tabular form indicate that the film formation could be carried out on various substrates. The physical and chemical properties of such semiconductors are comparable with the semiconductors prepared by other methods devices such as solar cells, photoconductors, detectors and solar selective.

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