COMPARATIVE STUDY OF ZNO BASED THIN FILM & NANOWIRE GAS SENSORS

M. Kashif*, U. Hashim*, Jamali. A.S**

ABSTRACT

ZnO nanowires are ideal building blocks for a wide range of nanoscale electronics, optoelectronics, and chemical sensing devices. The material properties change when the material is in nanowire form as compared to thin film or bulk. Nanowires are very promising for the development of new generation gas sensors. In nanowires, surface effects dominate due to increase of their particular surface that enhances the surface related properties like catalytic activity or surface adsorption. Sensitivity of nanowire to a particular gas increases if the catalyst is used to grow the nanowire. There are two methods for the synthesis of nanowire bottom up and top down. Both methods have their merits and demerits that will be discussed under the topic of nanowire synthesis and deposition methods. This paper presents the synthesis methods and comparative study on thin film and nanowire gas sensors.

Keywords: ZnO, nanowire, gas sensor, synthesis, adsorption.

1. INTRODUCTION

ZnO has received intense attention in the group of II-VI compound semiconductors due to its remarkable physical, gas sensing and optical properties. It has wide band gap (3.37 eV at room temperature), high excitation binding energy (60 meV), has a stable wurtzite structure with lattice spacing $a_0 = 0.325$ nm, $c_0 = 0.521$ nm and $c_0/a_0 = 1.602$ and its diverse growth morphologies make ZnO a key material in the fields of nanotechnology and wide band-gap semiconductors. The potential uses of ZnO is the fabrication of short wavelength devices, operating in the blue and ultra-violet regions of the electromagnetic spectrum, such as light emitting diodes, laser diodes and sensors. ZnO is one of the most widely applied oxide-gas sensor. ZnO gas sensing materials owe to their high chemical stability, low cost, and good flexibility in fabrication. ZnO sensor elements have been fabricated in various forms including single crystal [1-4], thin film [5-9]. The gas sensing mechanism involves chemisorptions of oxygen on the oxide surface followed by charge transfer during the reaction between chemisorbed oxygen reducing and target gas molecules. However, the physical and sensing properties of semiconductor gas sensors are directly related to their preparation e.g. particle size, sensing film morphology, and film thickness [10-15] as well as sensing film characteristics.

ZnO was pioneering material in gas sensing, though researchers preferred to extensively study SnO$_2$ because of its high gas sensitivity and its morphological and chemical stability. With the advent of modern nanotechnologies, zinc oxide has been rediscovered. ZnO has been successfully employed to detect various gases, such as H$_2$, NO$_2$, O$_2$, H$_2$S, CH$_3$CH$_2$OH and NH$_3$ [16-19]. This paper will discuss synthesis methods and deposition techniques and comparison between thin film and nanowire gas sensors.

Zinc oxide crystallizes in three forms: hexagonal wurtzite, cubic zinc blende, and the rarely observed cubic rock salt. The wurtzite structure is most stable at ambient conditions and thus most common. The zinc blende form can be stabilized by growing ZnO on substrates with cubic lattice structure. In both cases, the zinc and oxide centers are tetrahedral. The tetrahedral coordination is an indicator of covalent bonding (sp$^3$). Thus, ZnO lies on the borderline between being classified as a covalent or ionic compound.

2. SYNTHESIS METHODS & DEPOSITION TECHNIQUES OF 1D NANOSTRUCTURES

The preparations of nanomaterial are generally divided into two main categories which are top-down methods and bottom-up methods.

2.1 TOP DOWN

Top-down approach is based on standard micro fabrication methods with deposition, etching on planar
substrates in order to reduce the lateral dimensions of the films to the nanometer size. Top-down approaches usually utilize planar, lithographic techniques to transfer a pre-designed pattern to a substrate which can form complex high density structures in well-defined positions on substrates [20-21]. For example, Im et al. [20] synthesized ZnO nanowires using a complicated nanoscale spacer lithography method, which can be used to detect H2 and CO gases. Electron beam, focused ion beam, X-ray lithography, nano-imprinting and scanning probe microscope techniques can be used for the selective removal process. Top-down approaches have been widely used in the current microelectronic industry. They can produce nanostructures with very uniform shapes and electronic properties. With the passage of time and rapidly changes in the size of the devices the microelectronic industry advances towards ever smaller devices, this approach will soon reach their physical and economic limits, which motivates global efforts to search for new strategies to meet the expected demand for increased computational power as well as for integrating low-cost and flexible computing in unconventional environments in the future. The capability figures listed in Table 1 are based on majority of reported results and they are generally reproducible with certain type of equipment and process conditions [22].

Table 1: Direction nano fabrication techniques capabilities

<table>
<thead>
<tr>
<th>Technology</th>
<th>Capability</th>
</tr>
</thead>
<tbody>
<tr>
<td>Optical Lithography</td>
<td>∼ 30 nm</td>
</tr>
<tr>
<td>E-Beam Lithography</td>
<td>∼ 10 nm</td>
</tr>
<tr>
<td>Nanoimprint Lithography</td>
<td>∼ 10 nm</td>
</tr>
<tr>
<td>Scanning probe Lithography</td>
<td>∼ 20 nm</td>
</tr>
<tr>
<td>Reactive- Ion Etching</td>
<td>∼ 50 nm</td>
</tr>
<tr>
<td>Metal lift-off</td>
<td>∼ 10 nm</td>
</tr>
<tr>
<td>Focused Ion Beam</td>
<td>∼ 30 nm</td>
</tr>
</tbody>
</table>

The advantages of top-down approach are the use of the well developed technology of semiconductor industry and the ability to work on planar surfaces, on the other hand this approach has the disadvantages like their extremely elevated costs and preparation times. In top-down method nanoscale spacer patterning lithography method will be cover only.

(a) nanoscale spacer patterning lithography

Nanoscale spacer lithography is one of the most promising techniques that are used for the fabrication of aligned nanowires. That technique involves conventional lithography steps followed by RIE etching. This is an alternative way for the production of nanowires as compare to E-beam lithography. In this process sidewall/spacer was formed using sacrificial and etch stop layers. Sacrificial and etch stop layers were deposited using PECVD or LPCVD depends on the material. After that sacrificial layer was pattern using conventional lithography and etch by ICP process using suitable gases to etch that material or layer. In the next step ZnO or other metal oxide semiconductor material was deposited using ALD, RF sputtering or PLD process. The metal oxide semiconductor layer except for the spacer part was then removed by ICP etching with suitable gas discharges, so that the plasma damage to the metal oxide semiconductor spacer could be minimized. Finally, metal oxide nanowire arrays were obtained by etching the sacrificial oxide using the etch-stop layer. Figure 1 shows the steps of nanoscale lithography process for the fabrication of ZnO nanowire arrays [20].

Figure 1: Schematic diagram illustrating the fabrication processes of the ZnO nanowire device based on NSL: (a) thermal SiO2 deposition, (b) a-carbon deposition (etch-stop layer), (c) PECVD of SiO2 (sacrificial layer), (d) sacrificial layer patterning, (e) ZnO ALD, (f) top view after ZnO plasma etching, (g) sacrificial layer removal, and (h) ZnO nanowire device after metal electrode deposition.

(b) bottom-up

Bottom-up refers to methods where devices 'create themselves' by self assembly. In bottom-up approach, functional electronic structures are assembled from chemically synthesized nanoscale building blocks, represent flexible alternatives to conventional top-down methods. They can go far beyond the limits of top-down technology in terms of future physical and economic limits. [23-24]. Table 2 lists a host of 1-D metal oxide nanostructures grown from bottom-up approaches using different techniques. Bottom-up, consists of the assembly of molecular building blocks or chemical synthesis by vapor phase transport, electrochemical deposition, solution-based techniques or template growth. By using the bottom-up approaches the advantages are the high purity of the nanocrystalline materials produced, their small diameters, the low cost of the experimental set up together with the possibility to easily vary the intentional doping and the possible formation of junctions. The main disadvantage of this approach is their integration on planar substrates for the exploitation of their useful
Table 2: Synthetic Methods Developed for the Synthesis of 1-D Metal Oxide Nanoma Terial [25 – 28]

<table>
<thead>
<tr>
<th>Method (Vapor phase synthesis)</th>
<th>VLS Growth</th>
<th>VS Growth</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnO, SnO₂, In₂O₃, Fe₂O₃, MgO NWs, etc.</td>
<td>ZnO, SnO₂, In₂O₃, Co₃O₄, WO₃, MgO, Ga₂O₃ NWs, etc.</td>
<td></td>
</tr>
</tbody>
</table>

**Advantages:**
1. Typically produce high quality single-crystalline NWs with easy control over the diameter & length.
2. Capable of producing NWs on a large scale.

**Disadvantages:**
1. Need high temperature.
2. Complicated procedures are needed in some methods.

<table>
<thead>
<tr>
<th>Method (Solution phase synthesis)</th>
<th>Template-free growth</th>
<th>Template-assisted growth</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnO, SnO₂, V₂O₅, MnO₂ NWs, etc.</td>
<td>ZnO, SnO₂, TiO₂ NWs, etc.</td>
<td></td>
</tr>
</tbody>
</table>

**Advantages:**
1. Only need ambient temperature with reduced fabrication complexity and cost.

**Disadvantages:**
1. Typically difficult to control the diameter of NWs.
2. Template-assisted method usually produce polycrystalline NWs.

<table>
<thead>
<tr>
<th>Method (Other)</th>
<th>Electrospining etc.</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO₂, ZnO, SnO₂ NWs etc.</td>
<td></td>
</tr>
</tbody>
</table>

**Advantages:**
It usually requires complicated procedure and is difficult to control diameter.

(c) vapor phase growth
ZnO growth was performed in tubular furnace to obtain the proper temperature gradient in vapor phase growth method. The main advantage of the vapor phase process is the possibility to produce different type of materials in an easy way and with cheap deposition systems [29]. Once the source material is evaporated it is transported by a gas carrier towards the growth site where it nucleates. The process of nucleation can start from particles or catalyst. There are different categories for the vapor phase technique such as the self catalyzed vapor solid (VS), the catalyst assisted vapor liquid solid (VLS) and vapor phase transport (VPT), which are all based on the vapor phase technique but differ in the nucleation and growth mechanisms of the solid from the vapor species on the substrate.

2.2 CATALYST-ASSISTED VAPOR-LIQUID-SOLID METHOD (VLS)
In this method, the vapor species are generated and then condensed into a metal drop which acts as a catalyst for the growth. For ZnO, the morphology of the nucleated growth is generally wire or rod shaped. The diameter of the nanowires is controlled by the size of the liquid catalyst droplets (smaller catalyst yield thinner nanowires). Nanowires and nanorods produced by this method are remarkable for the uniformity of their diameter [30].

This method uses metals such as Au, Fe, Co and Ni as catalysts therefore this method is called catalyst assisted VLS method. The metal catalysts can be mixed with the source material or spread on the substrate where the nanowires grow. In either case, the metal catalyst is either patterned or self-organized into nanoparticles. These nanoparticles react with the source vapor forming solution droplets on the substrate that serves as a preferential site for absorption of reactant, since there is a much higher sticking probability on liquid versus solid surfaces. When the droplets become supersaturated, they are the nucleation sites for crystallization. Preferential 1D growth occurs in the presence of reactant as long as the catalyst remains liquid. During this process, the catalyst particle tends to remain at the tip of the growing nanowire (Fig. 2 ref 31). The size of the catalyst particles used to generate the nanowires depends on the preparation process. Typical methods include thin film deposition of the metal catalyst on the substrate by thermal evaporation or sputtering [32-33]. The metal thin film will cluster into small particles when heated up to the growth temperature. This typically leads to a wide distribution in nanoparticle diameter that is reflected in the diameter distribution of the resultant nanowires. The second approach is to deposit prefabricated mono-disperse catalyst nanoparticles on the substrate. Since the prefabricated nano-particles are uniform in size, nanowires can grow more uniformly in diameter [34].
2.3 SELF-CATALYZED VAPOR-LIQUID-SOLID
METHOD (VLS)

This technique is a catalyst-free method, during which the nanostructures are produced by condensing directly from the vapor phase. Therefore, morphology and alignment of the nanostructures are less controlled compared to the catalyst assisted VLS, in which the diameter of the nanowires is controlled by the size of the catalyst. However, it has been reported that under this synthesis more varied morphologies are possible due to the absence of constraints by the catalyst. Also, the technique has the advantage that contamination from the catalyst can be avoided during the growth process [30].

2.4 VAPOR-SOLID METHOD (VS)

Vapor solid (VS) growth takes place when the nanowire crystallization originates from the direct condensation from the vapor phase without using any catalyst. At the beginning the growth was attributed to the presence of lattice defects, but when defects-free nanowires were observed this explanation can not be any longer accepted. Vapor solid occur in many catalyst-free growth processes. Under high temperature condition, source materials are vaporized and then directly condensed on the substrate placed in the low temperature region. Figure 3 shows the set up for the vapor solid synthesis process.

![Figure 3: The setup of the vapor-solid (VS) synthesis process](image)

2.5 SOLUTION PHASE GROWTH

The solution-based catalyzed-growth mechanism is similar to the VLS mechanism, in this case a nanometer-scale metallic droplet catalyze the precursors decomposition and crystalline nanowire growth. These growth methods usually require ambient temperature so that complexity and cost of fabrication are considerably reduced. The variants of VLS growth in solutions SLS and supercritical fluid–liquid–solid (SFLS) growths provide nanowire solubility control over surface ligation, and smaller diameters. But the VLS growth in general produces nanowires of the best crystalline quality.

2.6 SOL–GEL

The sol-gel process is a wet-chemical procedure in which a solution of a metal compounds or suspension of very fine particles in a liquid (referred to as a sol) is converted into a semi-rigid mass (a gel). The sol-gel consists of mixture of solid materials suspended in a liquid solution. Gel occurs when the individual molecules form structures which then form molecules matrix network are same with the formation of semiconductor crystals but without ordered spacing. During thin film deposition, the parameters of deposition process such as deposition speed, deposition time, drying time and drying temperature will determine final material properties including structural, optical and electrical properties.

In the sol–gel process, a molecular precursor in a homogeneous solution undergoes a succession of transformations: (i) hydrolysis of the molecular precursor; (ii) polymerization via successive bimolecular additions of ions; (iii) condensation by dehydration; (iv) nucleation; and (v) growth [35]. Zinc precursors such as nitrate, chloride, acetylacetone and alkoxides such as ethoxide and propoxide, are used but the most often used is the acetate dehydrate. Metal salts are mostly used as a precursor because of their low cost, facility of use, and commercial availability. Inorganic salts like nitrates are often used, as precursors for sol–gel ZnO-based materials, even though their main drawback is related to the inclusion or difficult removal of anionic species in the final product [36]. An overview of the sol-gel process is presented in Figure 4.

The advantages of sol-gel technique are the ability to produce high-purity metal oxide because the organometallic precursor of the desired ceramic oxides can be mixed, dissolved in a specified solvent and hydrolyzed into a sol, and subsequently a gel; the composition can be highly controllable, the low temperature sintering
capability, usually 200–600°C; and last but not least the simple, economic and effective method to produce high-quality coatings. Despite its advantages, sol-gel technique never arrives at its full industrial potential due to some limitations, e.g., weak adhesion, low wear-resistance, and difficult controlling of porosity. In particular, the limit of the maximum coating thickness is 0.5 mm when the crack-free property is an indispensable requirement. The trapped organics with the thick coating often result in failure during thermal process. The substrate–layer expansion mismatch

nanostructures that can be released by dissolving the template. Nanoporous anodic aluminum oxide (AAO) membranes are the most extensively used templates for nanowire synthesis [38–41]. The pores inside the membrane are perpendicular to the surface and positioned in the form of a hexagonal lattice (See figure 5a). The size of the pore is proportional to the anodizing voltage.

For the nanowire synthesis, materials have to be filled into the nanoporous in some way. Electrochemistry is a powerful method for such applications and has been used limits the wide application of sol-gel technique.

2.7 TEMPLATE GROWTH

Template growth is another powerful method for the nanostructures synthesis for the electronic device applications. In the template growth method the template can serve as a container, the nanostructure grows within or around it; the shape of 1D nanostructure is complementary to the one of the chosen template. This technique provides a good control of the uniformity and on the dimension (owing a good control on pores dimensions and distribution), however the number of nano-wires that can be produced are limited by the template and the template removal can cause damage to 1D structure.

In this method materials are to be fill into a nanoporous template (mostly by electrochemistry) to form
to synthesize nanowires consisting of nonconductive metal oxides [38–42], metals [43–46], and semiconductors [47]. It is straight forward to fill metals and conducting polymers into the template by electrochemistry, while semiconducting and non-conducting materials can only be filled into the nanoporous in an indirect way.

There are also some other techniques to prepare metal oxides by electro-chemistry. For example, Zn (OH) x can be formed through electroplating Zn (NO₃)₂ solutions at an elevated temperature in the presence of O₂ [48]. The Zn (OH) x can also be filled into nanoporous templates and form ZnO crystal nanowires after a high temperature annealing.
nanowire-based gas sensors is the detection of small concentrations by measuring changes in electrical resistances in nanowires caused by the absorption or desorption of the chemical species or by phase changes in the nanowire [50].

Hyun-Wook Ra, fabricated ZnO nanowire sensor using nanoscale spacer patterning lithography in his paper he compare the response of nanowire sensor and thin film sensors. In his paper he shows the time dependence of the sensitivities of the ZnO nanowires obtained using the NSL technique and the ZnO thin film of thickness 100nm to various concentrations of H₂ and CO in the range of 500–5000ppm at 200 °C that is shown in figure 6. In the figure it indicates that both the ZnO nanowires and the thin films follow the fully general gas-sensing mechanism. The ZnO nanowires show a much higher sensitivity (about five times) compared to the ZnO thin film for both H₂ and CO. It is clear that the enhancement in gas sensitivity of the nanowires can be attributed to the higher surface-to-volume ratio than that of the thin film.

Figure 6: Sensitivities of the ZnO nanowires and ZnO thin film of thickness 100nm to different concentrations of a) H₂ and b) CO at 200 °C. [20].

In another paper jing wang & his team fabricate a nanowire sensor for gas detection using nanoimprint on SUS/SiO₂/PMMA trilayer. In his paper he fabricates three devices with different thickness. Table 3 that is taken from his paper shows the resistance and relative sensitivity of the three devices.

Table 3: Resistance and relative sensitivity for the three devices

<table>
<thead>
<tr>
<th>Samples</th>
<th>Resistance (Ω)</th>
<th>Sensitivity for NH₃ (%)</th>
<th>Sensitivity for NH₂ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thin film device</td>
<td>1x 10 exp3</td>
<td>-1.3</td>
<td>7.8</td>
</tr>
<tr>
<td>130 nm nanowire</td>
<td>177.9 x 10 exp3</td>
<td>-9.9</td>
<td>27.3</td>
</tr>
<tr>
<td>75 nm nanowire</td>
<td>916.4 x 10 exp3</td>
<td>-19.7</td>
<td>61.8</td>
</tr>
</tbody>
</table>
Comparative Study of ZnO Based Thin Film & Nanowire Gas Sensors

By comparing the values of three devices he mentioned that the resistance is anomalously large for the NW devices, especially for the narrower one. He indicate that this may be caused by the defects and traps generated in the RIE process which will make the channel partially depleted. Even with traps and defects, the NW devices still show a large enhancement in the sensitivity when compared to the thin film devices. The enhancement is even more obvious for the 75 nm one due to its higher surface to volume ratio.

From the above discussion it is very clear that the nanowire devices have more sensitivity as compare to thin film gas sensor and the gas sensitivity is dependent on the grain size or diameter of the nanowire. By decreasing the grain size the surface to volume ratio increase and surface to volume ratio play a major role in the gas sensing of nanowire gas sensors.

4. SUMMARY

This article reviewed the current progress in ZnO nanowire based gas sensors. For the gas sensing application sensitivity, selectivity and stability are the three important factors. Sensitivity depends on the grain size whereas selectivity depends on the appropriate selection for material for the gases of interest. Selectivity can be increased by doping the material with other selective sensing materials.

For the gas sensing grain size plays a major role in the sensitivity of the nanowire device as compare to thin film devices. The smaller the diameter of the nanowire greater will be the sensitivity. A great effort has been done to understand and control the growth process for the production of high quality nanowire with bottom up techniques as well as with top down techniques. In bottom up approach VLS mechanism is still widely employed for growing most of the nanowires produced nowadays. Solution-based techniques can be a promising alternative approach for mass production of metal oxide nanowires with good control of shape and composition. The main drawback of bottom up approach is the lack of full understanding of growth mechanism. Most of the methods are based on trial and error procedure and after getting nanowires transfer of single nanowire from one substrate to another substrate is very difficult and time consuming process.

On the other hand top-down approach has the advantages such as the use of the well developed technology of semiconductor industry and the ability to work on planar surfaces, while disadvantages are their extremely elevated costs and preparation times. Top-down approach there are various methods for the production of nanowires but now a days nanoscale spacer lithography is one of the promising method because of simple processing steps as compare to E-Beam lithography. By using spacer lithography one can get the nanowire of up to 40nm diameter. With the advancement of technology in the future it will be possible to go beyond this range.

REFERENCES


