Synthesis and Characterization of ZnO Nanowires using CVD Method

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Abstract— Gas sensors are devices that can convert the concentration of an analyte gas into an electronic signal. Zinc oxide (ZnO) is an important n-type metal oxide semiconductor which has been utilized as sensor for several decades. In recent years, there have been extensive investigations of nanoscale semiconductor gas sensors. In this research high-quality zinc oxide (ZnO) nanowires have been synthesized by vapour-Liquid-solid (VLS) method. Surface morphology, structural and optical properties of the ZnO nanowires were examined by scanning electron microscope (SEM), XRD analysis demonstrated that the ZnO nanowires has a wurtzite structure with orientation of (101) and the nanowires prepared at 900°C has a better crystalline quality than samples prepared at other temperatures. SEM results indicate that by increasing the oxidation temperature, the dimensions of the ZnO nanowires increase. The optimum temperature for synthesizing high density, ZnO nanowires was determined to be 900 °C.

Key words: CVD Method, ZnO Nanowires, Synthesis

I. INTRODUCTION

In recent years, low-dimensional systems have attracted tremendous research interest for nanosensor applications due to their gas sensitivity, ultraviolet (UV) photo response, optical transparency in the visible region, etc. [1–14]. In particular, quasi-one-dimensional (Q1D) nanowires/nanorods are promising as a low-cost material for high-speed UV photoconductive nanoscale detectors and gas sensors [3, 7–14]. Current research efforts are focused on the UV light and chemical sensing properties of metal oxide nanowires, such as zinc oxide (ZnO), tin oxide (SnO_2), indium oxide (In_2O_3), aluminum oxide (Al_2O_2), gallium oxide (Ga_2O_3), and vanadium oxide (V_2O_5)[5,7,15–17]. In particular, several authors have demonstrated that zinc oxide nanowires (NWs) have unique properties, such as high sensitivity under ambient conditions, and that they are a potential candidate for use as a sensing material [7,8,15–17]. In addition, ZnO is a low-cost material which is simple to fabricate, making it attractive for research and industrial applications. Recently, Tien et al. [18] used Pt-coated ZnO nanorods as sensors capable of detecting ppm concentrations of hydrogen at room temperature. Heo et al.used Au islands for site-selective growth of ZnO nanowires by Molecular Beam Epitaxy (MBE) at 600C. Wang et al.[20] studied the response of Pd-coated ZnO nanorods to H2at ppm levels in $N_2$and found them to be suitable for practical applications in hydrogen selective sensing at room temperature. In another study by Son et al. [21] ZnO nanowires synthesized by pulsed laser deposition (PLD) were used, and sensitivity to low concentrations of ethanol was reported. ZnO nanorods/nanowires synthesized by different techniques were also reported as sensors of a variety of gases like ammonia, formaldehyde, hydrogen, nitrogen dioxide, and carbon monoxide [7,8,19]. According to previous reports the sensitivity of ZnO to gas could be affected by nanostructure, surface defects and post growth annealing in H_2or O_2 ambient. At the same time it is necessary to mention that many researchers dealing with the growth of ZnO nanowires use gold nanodrops as a catalyst. Although the ensembles of nanowires obtained in this manner are quite uniform in size, gold is always present as an impurity and alters the crystalline and optical properties of ZnO, possibly affecting also its sensing capabilities and long term stability. Therefore, to improve the emissivity and electrical properties of ZnO nanowires, one has to consider the possibilities of their synthesis without depending on metal catalysts. Here, we present the controlled synthesis of ZnO nanowires by chemical vapor deposition (CVD) without the use of a catalyst. In addition, we report details related to the systematic characterization of the as synthesized zinc oxide nanomaterial for sensor applications. To investigate the sensing properties of the CVD-fabricated ZnO nanowires and their feasibility for nanoscale multifunctional sensor applications, we used a focused ion beam (FIB) set-up to deposit metal electrodes for external contacts. A nanodevice is fabricated from an individual zinc oxide nanowire and characterized.

II. EXPERIMENTAL DETAILS

A. Thermal Evaporation:

Nanowires and some interesting morphologies of nanostructures such as nanoribbons, nano tetrapods and comb-like structures can be fabricated by a simple method of thermal evaporation of solid source materials. The experimental setup is extremely simple as shown in Figure.1. The temperature gradient and the vacuum conditions are two critical parameters for the formation of nanowires by this method. Typical materials suitable for this fabrication are metal oxides, e.g., ZnO, SnO_2, In_2O_5, VO, etc. and some semiconductors. The fabrication of these nanowires is simply through evaporating commercial metal oxide powders at elevated temperatures under a vacuum or in an inert gas atmosphere with a negative pressure. Nanowire products form in the low temperature regions where materials deposit from the vapour phase. It is believed that the nanowires are generated directly from the vapour phase in the absence of a metal catalyst, and this process is often called vapour–solid (VS) growth. To generate the vapour phases of the source materials, vacuum conditions are sometimes needed.

This is because some materials may not sublimate in the normal atmosphere. An effective way to generate the vapour source materials in a normal atmosphere is to add additional materials to react with the source materials. For example, ZnO powder does not sublimate in a normal atmosphere at 1000°C. By adding carbon powder to react with the ZnO source, Zn or Zn-suboxide vapour phases can be easily generated at 1000 °C. Various forms of ZnO nanostructures grow in the low-temperature zone. In this case, vacuum conditions, carrying gases and catalysts are all unnecessary .The temperature is critical for the formation of different forms of ZnO nanostructures.

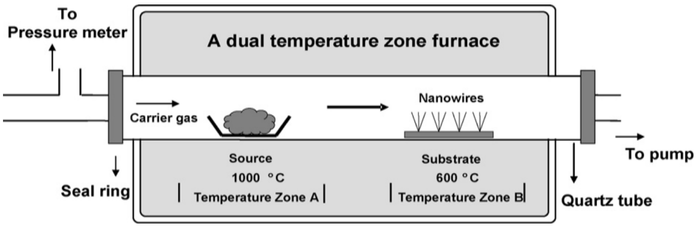

Fig. 1: A simple experimental setup of the thermal evaporation method for synthesizing ZnO nanostructures. The source material is ZnO or a mixture of ZnO and carbon. Different forms of the ZnO nanostructures, e.g., nanowires and ribbons, grow in different temperature zones.

B. Characterization Results:

1) Scanning Electron Microscopy (SEM) And Energy-Dispersive X-Ray Pectroscopy (EDX):

Scanning electron microscopy (SEM) is a highly important tool for the investigation of the surface morphology of nanostructures. By employing it we can investigate the diameter, length, thickness, density, shape and orientation of the nanostructures. The maximum resolution of the SEM was up to 10 nm. This can be clearly seen from these SEM images that fabricated ZnO nanorods and nanotubes were well aligned in figure 2. hexagonal and vertical with high density. The fabricated nanorods and nanotubes uniformly spread all over the substrate. This can be seen from the SEM images that the diameters of our as fabricated ZnO nanorods and nanotubes were around 150-250 nm and the length of the both were around 1.2 µm.

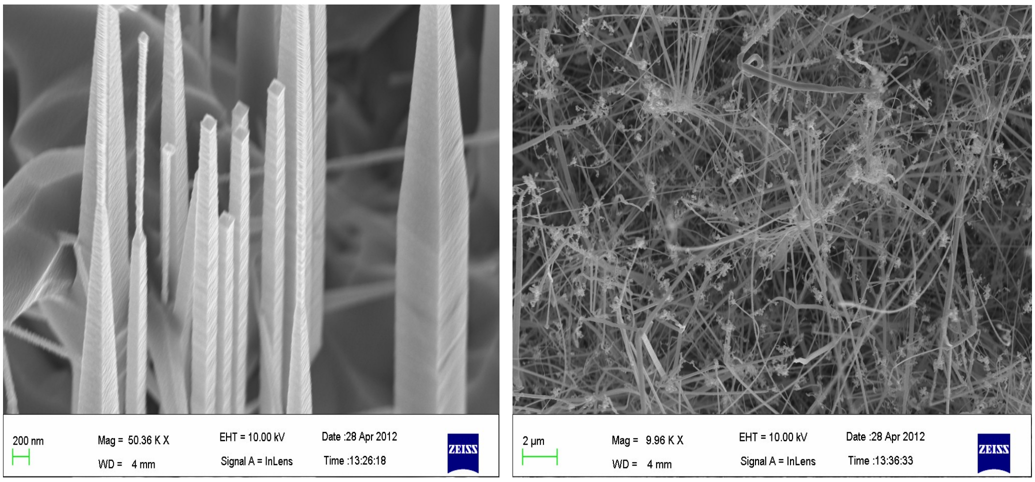

Fig. 2: Scanning electron microscope (SEM) images of some ZnO nanowire fabricated on different substrate using vapour growth technique.

The SEM also has energy-dispersive X-ray spectroscopy (EDX) that analyzes the chemical composition of object nanostructures. Figure 3 shows a typical EDX spectrum of ZnO nanowires on gold coated plastic substrate, which indicates that the as-grown samples are indeed ZnO in figure 3.

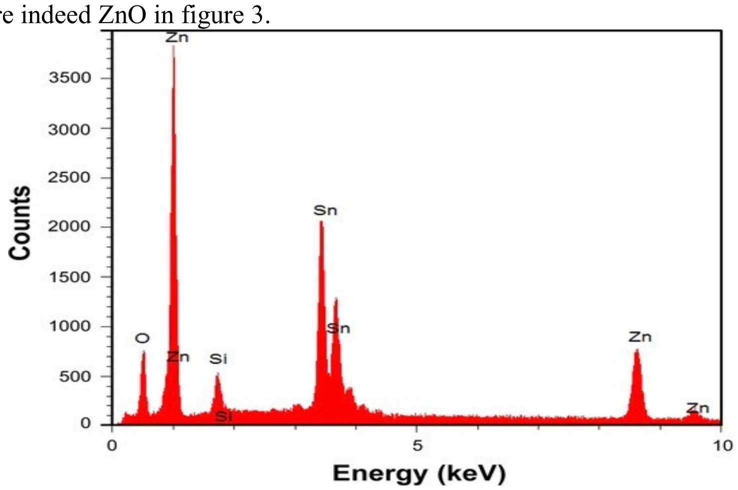

Fig. 3: EDX spectrum of ZnO nanowires on a gold coated silicon substrate

C. X-ray diffraction:

The as-prepared ZnO nanowires on the Si substrate were characterized by X-ray diffraction (XRD) using a Rigaku 'D/B max' X-ray diffractometer (Cu Ka radiation source with l=1.54178 A˚). The operating conditions were 30 mA and 40 kV at a scanning rate of 0.048/s. The morphology and chemical composition of the samples were studied using a VEGA TESCAN TS 5130MM scanning electron microscope (SEM) equipped with an Oxford Instruments INCA energy dispersive X-ray (EDX) system. Transmission electron microscopy (TEM) was performed with a FEI Tecnai F30 TEM at an accelerating voltage of 300 kV in figure 4.

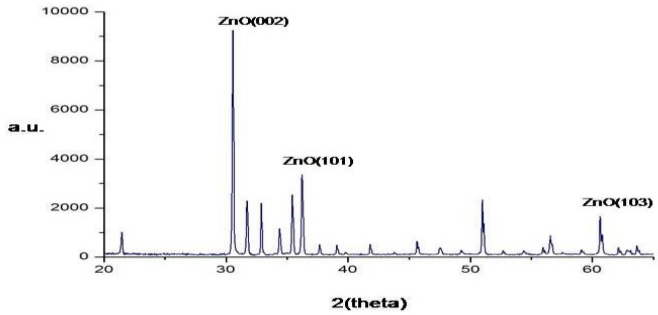

Fig. 4: XRD spectra of ZnO nanowire grown on silicon substrates.

III. CONCLUSIONS

We have developed a CVD technique to grow high quality ZnO nanowires with diameters. Through the control of the oxygen/zinc ratio, vertically aligned nanowires have been grown. The shape and the size of the ZnO nanorods were found to depend on the position of the substrate in the growth zone. This dependence is explained by rapid oxygen consumption in the reaction zone. The structural and chemical quality of the ZnO nanowires was verified through SEM. The obtained nanowires are transferable to another substrate with prepatterned external contacts. A single ZnO nanosensor was fabricated using a FIB set-up. FIB lithography was used to pattern metal electrodes contacting both ends of a single ZnO nanowire. The individual ZnO nanowires can be used as a sensing material in nanosensors with a higher response to hydrogen gas at room temperature in comparison with previous reports.

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