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Characterization and Modeling of Catalyst-free Carbon-Assisted Synthesis of ZnO Nanowires

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ABSTRACT

ZnO nanowires have been widely studied due to their unique material properties and many potential applications in electronic and optoelectronic devices. Many growth processes have been developed to synthesize ZnO nanowires. It is critically important to develop predictive process models so as to maximize the output of the nanowire synthesis. Here we report a method to characterize, quantify, and model a catalyst-free carbon-assisted ZnO nanowire growth process. Two key factors were identified for the synthesis conditions, which are reaction temperature and flow rate. Based on a factorial design method, we conducted experiments with different combinations of the two factors to study their effects on the process output (i.e. density of the nanowires), which was evaluated by a scanning electron microscope (SEM). The experimental results were analyzed using ANOVA test, and then a semi-empirical model was built to correlate the ZnO nanowire output with synthesis conditions. This model was able to describe the ZnO nanowire density with respect to synthesis conditions, which can provide guideline for synthesis parameters selection and process optimization.

1. Introduction

ZnO nanowire is an important semiconducting and piezoelectric nanomaterial [1] with a large exciton binding energy, a wide bandgap and excellent mechanical properties [2,3]. They have received significant attention in recent years because of their potential applications in electronic and optoelectronic devices, such as solar cells [4,5], field emission devices [6,7], transistors for transparent and flexible electronics [8,9], photodetectors [10], light-emitting diodes [11] and piezo nanogenerators [12–14].

The methods to synthesize ZnO nanowires can be classified into two categories: vapor phase synthesis and solution phase synthesis. A number of vapor phase techniques have been developed including vapor liquid solid (VLS) growth [15–18], chemical vapor deposition (CVD) [19–22], metal organic chemical vapor deposition (MOCVD) [23–26], physical vapor deposition (PVD) [27–30], molecular beam epitaxy (MBE) [31–34], pulsed laser deposition (PLD) [35–38], and metal organic vapor phase epitaxy (MOVPE) [39–41]. Among these methods, VLS is the simplest vapor phase technique to synthesize ZnO nanowires, especially in large scale [42]. During the VLS growth, the quality and growth behavior of ZnO nanowires are affected by many factors including oxygen partial pressure, thickness of the catalyst layer and chamber pressure. Catalyst-free metal-organic chemical vapor deposition (MOCVD) has been applied to produce high-purity ZnO nanowire as the impurities introduced by catalysts have been eliminated. Also, the growth temperature is lower than the growth temperature in VLS processes [43]. Solution phase synthesis has many advantages over vapor phase synthesis, including low temperature, low cost, good scalability. Moreover, many substrates can be chosen for solution phase synthesis. Solution phase synthesis methods including hydrothermal method [44–50], microemulsion [51], and ethanol base methods [52]. Due to oxygen vacancies, ZnO nanowires synthesized by hydrothermal methods have more crystalline defects [53], which allow nanowires exhibit visible light photo catalysis even without doping with transition metal. Statistical design of experiments have been applied to the hydrothermal deposition process to improve growth performance and quality of the ZnO nanowires [54]. Besides ZnO nanowires, kinetics modeling and statistical modeling have been studied for many other nanomaterials [55–57].

In this work, we developed a method to characterize and model a catalyst-free carbon-assisted ZnO nanowire growth process. To synthesize ZnO nanowires using the CVD method, ZnO patterns

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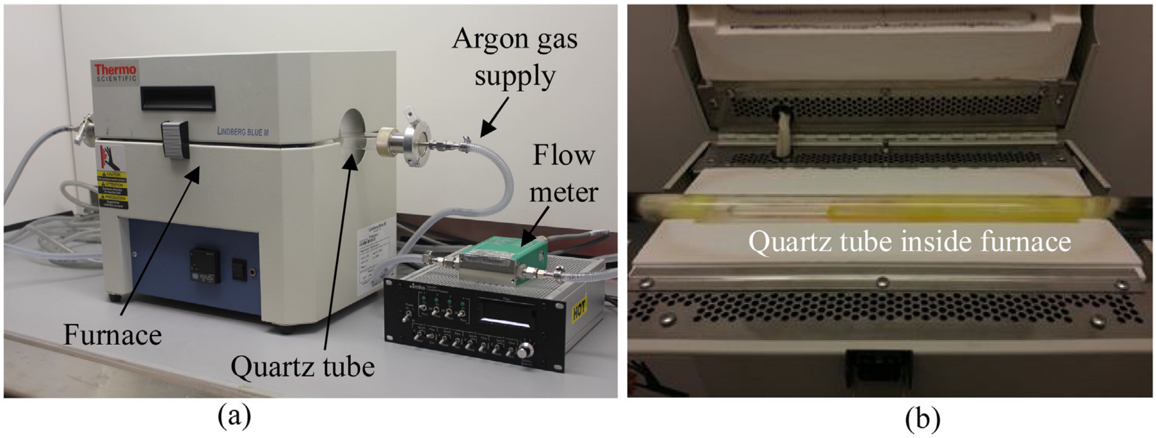

Fig. 1. (a) Chemical vapor deposition system (b) Furnace with quartz tube inside.

were printed onto a silicon substrate using a novel electrohydrodynamic (EHD) printing process. We found that two factors, temperature and flow rate, significantly affect the ZnO growth process. To correlate the growth process conditions with the process throughput, we conducted experiments with different synthesis conditions base on blocked factorial design method, and quantitatively characterized the process throughput (i.e. nanowire density) using scanning electron microscope (SEM) images. The Analysis Of Variance (ANOVA) tests were performed to evaluate the effects and significance of the process parameters (i.e. temperature and flow rate) on the process throughput. A modified two-dimensional elliptical Gaussian model was developed to describe the relationship between the process parameters and process throughput, so as to quantitatively predict the output (i.e. throughput) of ZnO nanowire growth process. The results from the model agreed very well with the experimental results.

2. Experimental methods

A CVD system was developed for the growth of ZnO nanowires, as shown in Fig. 1, which includes a temperature-controlled furnace and a gas flow control system. The furnace including a quartz tube and a temperature controlled heating element was used to heat up the sample and chemical reactants to the desired temperature for nanowire growth. A quartz tube with the inside diameter of 22 mm and the length of 100 cm was placed inside the high-temperature tube furnace.

To selectively grow ZnO nanowires on the substrate, ZnO patterns were printed onto the silicon substrate by the EHD printing process. The ZnO ink was obtained by mixing 1 weight percent (wt%) of ZnO nanoparticles and 5 wt% of polyvinylpyrrolidone (PVP) with ethanol, followed by ultrasonication for two hours. The PVP was used as the surfactant to prevent the aggregation of the ZnO nanoparticles in the ink. During the EHD printing, a voltage of 1500 V between the nozzle and the substrate was applied to initiate the printing process. The printed patterns on the substrate were dried in air and then transferred to an oven for 3 hours at 450 °C to decompose the PVP coating on ZnO nanoparticles. The resulting substrate with the ZnO patterns was used as the collector substrate for ZnO nanowire growth process.

In the growth process, ZnO power and graphite powder were mixed with 1:1 ratio as reactants. The reactant was placed in the quartz boat located in the center of the furnace. The collector substrate (i.e. a silicon die with the printed ZnO patterns) was located near the tube outlet. An Argon gas flow was supplied to the tube during growth process, with mass flow rates between 1 sccm and 100 sccm. The pressure of furnace and the growth time were set to be 100 Torr and 30 minutes respectively. After the temperature of quartz boat reaches reaction temperature, the ZnO is reduced by graphite, and gaseous products will be produced including Zn vapor and CO. As the printed ZnO patterns contain huge amount of ZnO nanoparticles with large specific surface area, which will serve as nucleus sites for nanowire growth. Once the gaseous products are transported to cooler area where the collector is located by Argon gas flow, the Zn vapor is deposited on the surface of the nucleus sites and re-oxidized, resulting in the growth of ZnO nanowires.

3. Results and discussion

High-resolution ZnO patterns were successfully printed onto the silicon substrate using EHD printing process [58–60] of liquid ink with ZnO nanoparticles. The printed ZnO pattern was shown in Fig. 2(a) with the smallest line width about 25 μm. With the high-resolution ZnO patterns, ZnO nanowires were selectively grown on the substrate using CVD process, as shown in Fig. 2(b). With these selectively fabricated patterns, it is easier to quantitatively measure the density of the nanowires and to study the effect of the process parameters (such as temperature gradient) to the nanowire growth process.

Based on our observations from pre-experiments, a few synthesis parameters possibly affect the throughput of ZnO nanowire growth process, including furnace temperature, Argon flow rate, and the location on the substrate along the temperature gradient direction. Significant difference of the nanowire growth results at different process conditions and locations was clearly observed, which result in different nanowires density (i.e. productivity) on the substrate as shown in Fig. 3.

To control and optimize the synthesis process for achieving high throughput of ZnO nanowires, we need to understand the relationship between the produced ZnO nanowires and the corresponding synthesis parameters. To analyze and model the process, we first quantitatively characterize the throughput of the produced nanowires. The substrate after growth process was imaged by Scan Electronic Microscope (SEM). The density of the produced nanowires is used to evaluate the throughput of the nanowire growth process. As it is time consuming to enumerate all the synthesis conditions experimentally, we applied Blocked Fractional Factorial Designs method to reduce unnecessary experiments. Based on our pre-experiments, furnace temperature is set to range from 920 °C to 1000 °C, flow rate varies from 60 to 100 sccm, and substrate dimension along the temperature gradient direction is about 14 mm.

We design experiments to cover all the synthesis conditions, including the entire temperature and flow rate range on the whole