Center for Environmental Research and Technology

Synthesis of ZnO Nanostructures with Gradated Morphologies

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Objectives

1) To synthesize diverse morphologies of ZnO nanostructures under low temperature
2) To control the length, diameter and morphology of one-dimensional structures by adjusting experimental parameters
3) To prevent the oxidization of Zn precursor, by protecting it from oxygen
4) To investigate the relationship between the morphology and partial vapor pressure difference on a single substrate

Abstract

ZnO is a crystalline material with diverse morphology, large bandgap and high visible transparency. It is a suitable material for photovoltaic devices such as dye-sensitized solar cells.

In our lab, we have synthesized ZnO crystals at low temperature by protecting the precursor boat from oxygen gas during synthesis, effectively preventing the premature oxidization of Zn precursor before it reaches the deposition substrate. Furthermore, by optimizing the experimental parameters during synthesis, different morphologies of ZnO have been achieved.

Our work is focused at identifying the underlying factors that lead to the synthesis of different ZnO structures under different conditions, understanding the growth mechanism of each synthesized structure and investigating their application for photovoltaic devices.

Background

Zinc Oxide (ZnO)

Zinc oxide is naturally a wide-bandgap n-type semiconducting material due to the oxygen vacancies and zinc interstitials (Figure 1). ZnO has several crystal structures. Hexagonal wurtzite (Figure 2) is the most stable at ambient conditions and thus most common, while Zinc blende is stable only when grown on a cubic lattice substrate. Other significant properties of ZnO are listed below.

- Visible light transparency: Since the bandgap of ZnO is wide, it absorbs UV light but not visible light.
- Piezoelectricity and pyroelectricity: There is no inversion symmetry in the wurtzite crystal structure, so that it causes piezoelectricity and pyroelectricity in wurtzite ZnO.
- Photocatalytic property: ZnO is known as a photocatalyst because it absorbs UV light, and excited ZnO can be a medium for redox reaction. Although its photocatalytic activity is less than TiO_2, it is of interest because it can be easily synthesized in higher dimensional structures.

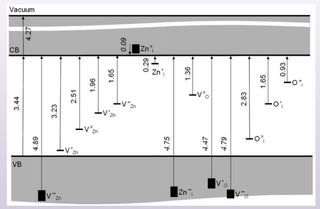


Figure 1. Calculated donor defect levels in ZnO.
Faraday Discuss., 2007, **134**, 267–282

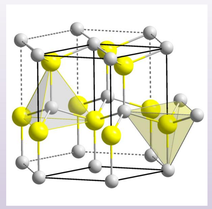


Figure 2. Wurtzite crystal structure.
http://en.wikipedia.org/wiki/Zinc_oxide

Chemical Vapor Deposition

In this work chemical vapor deposition (CVD) is used as the synthesis route to synthesize the ZnO nanostructures. Figure 3 shows the schematic of the CVD experimental setup. In contrast with physical vapor deposition (PVD) methods, such as sputtering or evaporation, CVD is accompanied by a chemical reaction; allowing for greater control of the material stoichiometry, applicability and step coverage. Additionally, in the CVD method, the starting material used for deposition is in the gas phase as a precursor instead of the target material itself. The mechanism for deposition of the target material near the substrate is the chemical reaction between the two different gas phase precursors. Therefore, a variety of chemical reactions are possible depending on the starting materials chosen and the experimental conditions.

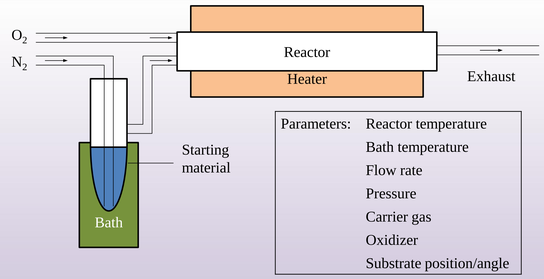
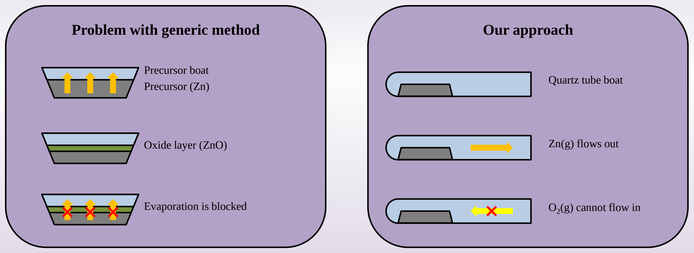


Figure 3. Schematic illustration of CVD process.

Research Approach

Preventing Oxidization of Zn Precursor

In the typical CVD process, the precursor is placed on a boat and the precursor evaporates by heat. During this process, oxygen oxidizes the precursor before it evaporates and a thin oxide film layer forms on the top of the precursor. The oxide layer blocks the evaporating precursor, so that the partial pressure of the precursor vapor is decreased and uncontrollable. Preventing the oxidization of Zn precursor before it evaporates is one of the main strategies to keep the vapor flow constant and controllable during synthesis. In this research, a thin quartz test tube is used as the precursor boat instead of bowl-shaped boat.



Adjusting Experimental Parameters

Experimental parameters such as temperature, pressure, flow rate, and substrate position are adjusted to find the optimal condition to synthesize vertically grown ZnO nanostructures with controllable dimensions and morphology.

Experimental Work

Experimental Conditions

- Substrate: Fluorine-doped tin oxide (FTO)
- Pressure: 10^{-3} torr low-vacuum with mechanical pump
- Precursor: Pure Zn powder
- Carrier gas: 50-200 SCCM nitrogen gas
- Oxidizer: 2-10 SCCM oxygen gas
- Temperature: 430-550 °C
- Substrate position: ¼ to 1½ inch from boat; top facing

Synthesis Process

Pre-cut FTO substrate (2 x 2 cm) is cleaned by ultra-sonication in detergent-water, acetone, and 2-propanol for 15 min each. 0.5 gram of pure Zn powder, as precursor, is placed in a small and long quartz test tube as a boat, and positioned inside the tube furnace. The cleaned substrate is placed at a pre-determined distance away from the boat along downstream. Low-vacuum is achieved by a mechanical pump and carrier gas N_2, and oxidizer O_2 are flowed. The reactor is heated up to 520°C with 15°C/min ramping rate and the reaction temperature is maintained for 30 min.

Characterization

- SEM and EDS are used for analyzing physical structure, morphology, and elemental composition
- XRD is used to study crystal structure and crystallinity
- Raman spectroscopy is used for carrying out semiconducting impurity analysis

Results

SEM Characterization

The synthesized ZnO film grown on a FTO substrate shows a circular pattern, characterized by a gradually changing color in the radial direction. Therefore, a series of SEM images are taken at different spots within the substrate to compare and contrast the morphology and dimensional characteristics. The images are shown in Figure 4 (each spot has a 2 mm distance from each other).

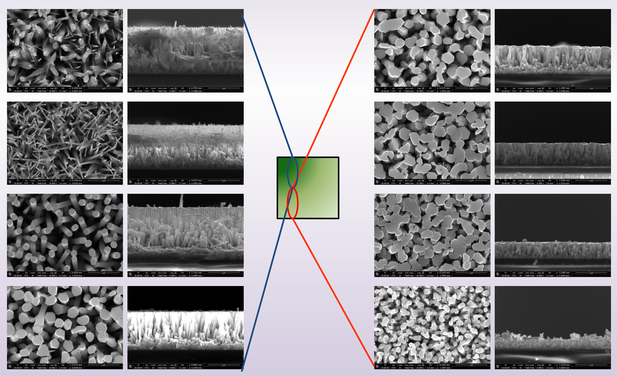


Figure 4. SEM images taken at different spots within a single FTO substrate.

X-ray Diffraction (XRD) Analysis

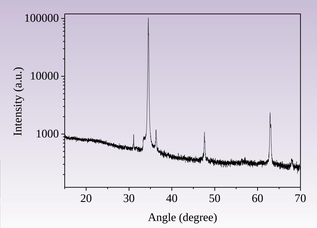


Figure 5. XRD pattern of synthesized ZnO film.

Peaks in Figure 5 are observed at 31.0°, 34.5 °, 36.3 °, 47.6 °, 63.0 ° and they refer to (100), (002), (101), (102), (103) in wurtzite structure, respectively.

The dominant peak at 34.5 ° is much higher than the peak of powder XRD, which means the one-dimensional structures are grown along z-axis.

Raman Spectroscopy

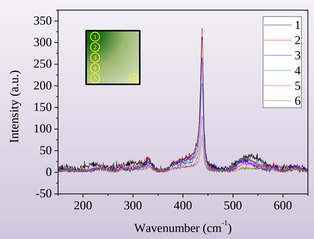


Fig 6. Raman spectra at different spots.

In Figure 6, the Raman spectra show peak shift and intensity difference based on the sampling position (i.e. 1, 2, 3, 4, 5, and 6) on the deposition substrate. The observed peak shift and intensity change is due to the non-stoichiometric nature of the as-synthesized product. The observed non-stoichiometry is due to the different oxygen vacancy concentrations derived from the difference in partial vapor pressures at the deposition substrate during synthesis.

Conclusion

Summary

In this research, we have successfully synthesized ZnO nanostructures exhibiting a gradated morphology. By protecting the precursor from oxidization, ZnO has been synthesized under low-temperature, and experimental conditions such as vapor pressure has become more controllable. The synthesized ZnO nanostructures have been characterized via electron microscopy, x-ray diffraction, and Raman spectroscopy. Experimentally, it was observed by SEM characterization that the morphology is gradually changing in radial shape. The wurtzite crystal structure grown along the z-axis is confirmed by XRD results, showing that the dominant peak is caused by a facial preference parallel to the (002) plane. The identified mechanism for the synthesis of the gradated nanostructures is the partial vapor pressure of each reactant (zinc vapor and oxygen gas) near the deposition substrate.

Future Plans

1) Characterization: Other characterization techniques such as TEM, and photoluminescence measurements will be conducted to further analyze the crystal structure, which will be crucial to determining the relationship between the partial vapor pressure ratio of Zn and O_2 during synthesis.
2) Application: Synthesized ZnO will be applied on semiconductor-based devices such as dye-sensitized solar cells, phototransistors, photocatalysts, and piezoelectric devices.
3) Synthesis: Morphology and crystal structure of ZnO will be further controlled and optimize for each applicable device. Not only 1-D structure, but also 2-D sheet or ribbon, 3-D dendrite, and core-shell hybrid structure will be synthesized.

Acknowledgement

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