Center for Environmental Research and Technology

Template-free and Low Temperature CVD Synthesis of Vertically Aligned 1-D Nanostructures for Photovoltaic Devices by Precursor Oxidation Protection

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Abstract

Zinc oxide (ZnO) is a crystalline material with diverse morphology, large bandgap and high visible light transparency. All of these properties make ZnO a suitable material for applications in optical devices such as photovoltaic cells and photodiodes. Particularly, for photovoltaic applications, it is necessary to grow ZnO on a transparent conducting oxide (TCO) substrate. In this work, vertically aligned 1-D ZnO has been synthesized on a TCO substrate through chemical vapor deposition (CVD). Although previously ZnO nanostructures have been synthesized at low temperatures through the use of a Zn powder precursor, oxidation of the precursor during synthesis remains a significant limiting factor, limiting the length of vertically aligned 1-D structures to below 6 um.

In this work, ZnO is synthesized under lower temperatures through the prevention of precursor oxidation and control of Zn vapor fluid dynamics. Partial pressure of Zn vapor - a significant factor in the morphology and quality of product - is controlled and maintained. In our results, we present the morphology and crystal structure of ZnO synthesized at different conditions observed by scanning electron microscopy (SEM) and x-ray diffraction (XRD). The growth mechanism of each structure in regards to the partial pressure of Zn vapor is discussed. We also demonstrate the fabrication of dye-sensitized solar cell (DSSC) with synthesized 1-D ZnO as a photoelectrode and analyze the photovoltaic characteristics and performance.

Introduction

❑ Zinc Oxide (ZnO)

- Wide-bandgap semiconductor
- Transparent, high electron mobility
- Hexagonal wurtzite
- Piezoelectricity, pyroelectricity characteristics

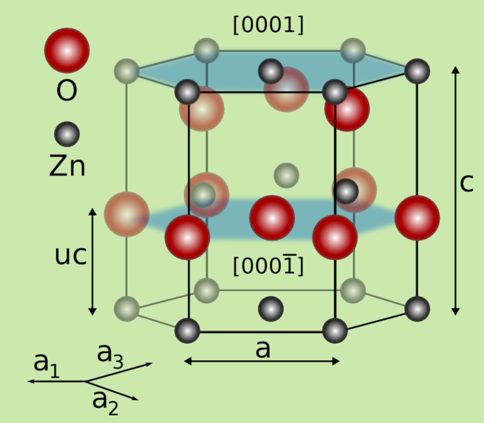


Figure 1. Crystal structure of wurtzite ZnO

http://www.theochem.ruhr-uni-bochum.de/~joerg.behler/zno.htm

❑ Chemical vapor deposition (CVD)

- High-purity, high-performance solid product
- Flexible conditioning
- Cost-effective
- Good step coverage

❑ Dye-Sensitized Solar Cells

- Low cost and simple process
- High efficiency
- Aesthetically pleasant
- Suitable for BIPV
- TCO | TiO_2 : dye | electrolyte | TCO structure

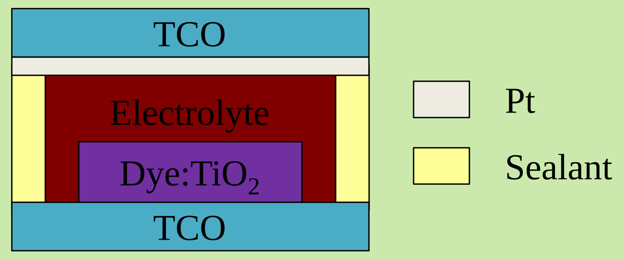


Figure 2. Structure of DSSCs

Experiments

❑ CVD synthesis process

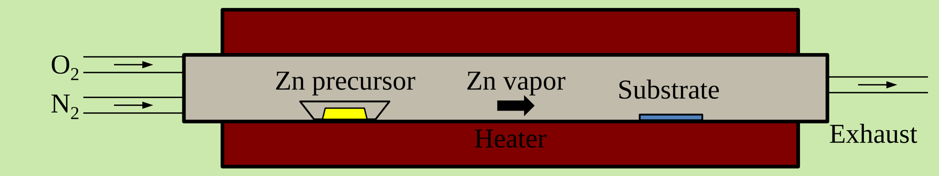


Figure 3. Schematic drawing of CVD synthesis system

❑ Precursor oxidation protection

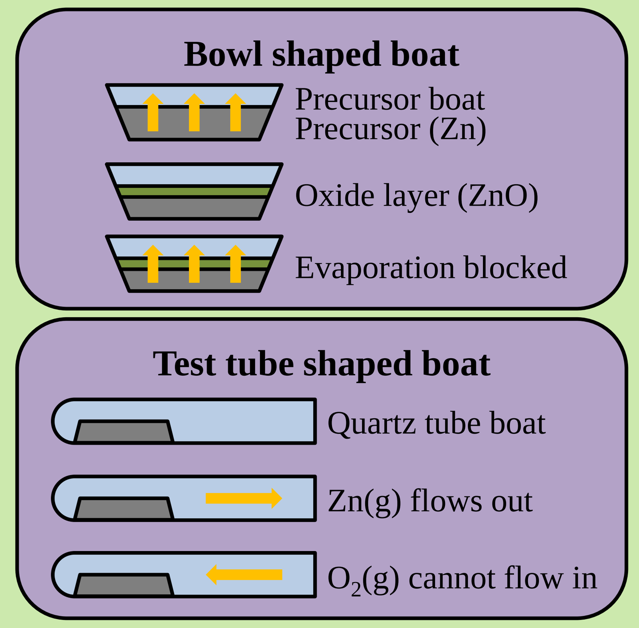


Figure 4. Comparison of two different boats

❑ Experimental conditions

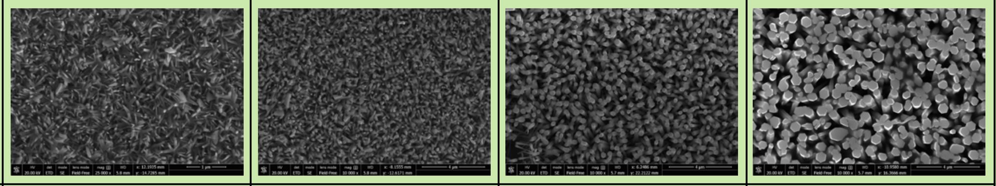
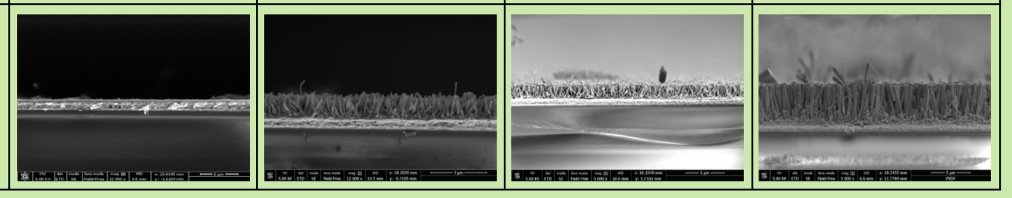
Table 1. List of controllable parameters and range of CVD synthesis

Controllable parameters	Conditions range
Precursor temperature	450 - 600°C
Ramping/Reaction time	10 - 60 min / 30 - 120 min
Pressure	Atmospheric pressure ~ 10^{-3} torr
Carrier gas	Nitrogen (N_2)
Oxidizer	Oxygen (O_2)
Flow rate	N_2: 50 - 200 SCCM / O_2: 0 - 10 SCCM
Precursor-Substrate distance	0 - 2 cm
Substrate orientation	Parallel to gas flow

Results and Discussion

❑ Morphology characterization

Table 2. List of SEM images of synthesized ZnO under different temperature and boat

Temperature	470°C	470°C	500°C	500°C
Boat Shape	Bowl	Test tube	Bowl	Test tube
Surface				
Cross-section				

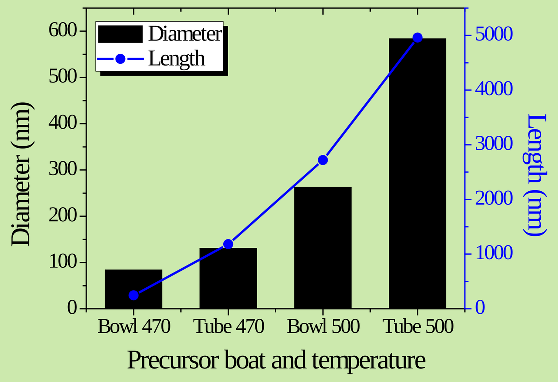


Figure 5. Dimensions comparison chart

ZnO nanostructures were synthesized by using two different precursor boats, with different shapes, under different temperatures. The morphology and dimensions of the material were characterized by SEM. As shown in Figure 5, the shape of precursor boat plays a pivotal role in the growth of the ZnO. ZnO grown using a tube-shaped boat was thicker and longer than that grown using a bowl-shaped boat, and it was even grown under lower reaction temperature.

❑ Crystal structure characterization

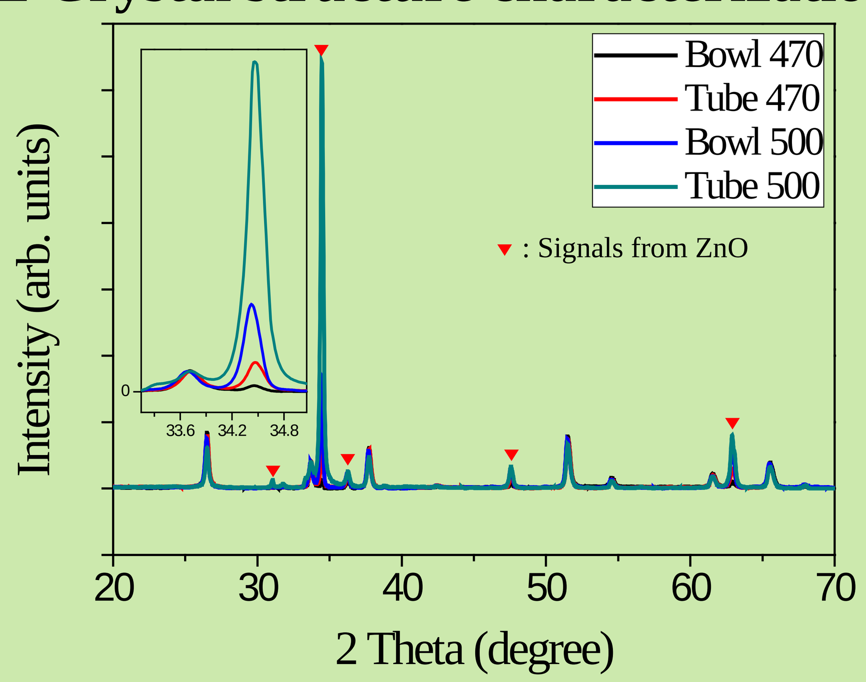


Figure 6. XRD patterns of synthesized ZnO

Table 2. List of XRD peak positions and corresponding miller indices

Peak position	26.51	31.06	33.71	34.46	36.27	37.73
Peak source	FTO	ZnO	FTO	**ZnO**	ZnO	FTO
Miller indices	(110)	(100)	(101)	**(002)**	(101)	(200)
Peak position	**47.56**	**51.50**	**54.53**	**61.51**	**62.90**	**65.50**
Peak source	ZnO	FTO	FTO	FTO	ZnO	FTO
Peak position	(102)	(211)	(220)	(310)	(103)	(301)

❑ Photovoltaic characteristics

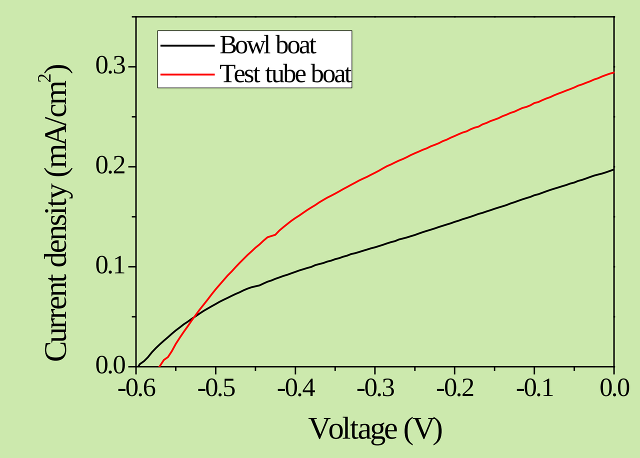


Figure 7. Photovoltaic I-V characteristics of DSSCs using synthesized ZnO under 450°C with different precursor boat

In the XRD pattern, the strongest peak from ZnO was observed at 34.46° which is from the (002) plane. That plane is perpendicular to the z-axis in the hexagonal wurtzite crystal structure. This observation indicates that the synthesized ZnO was grown preferentially along the z-axis. The ratio of the peak at 34.46° was increased significantly when the tube shaped boat was used, which means using the tube shaped boat assists ZnO to grow along z-axis and form high aspect ratio structures.

The photovoltaic characteristics of the 1-D ZnO synthesized with the test tube shaped boat shows better overall efficiency due to the higher surface area and density of the material.

Conclusion

In this work, we have synthesized vertically aligned 1-D ZnO on transparent electrode without template by CVD. Morphology and dimensional characteristics were characterized by SEM, and high crystallinity wurtzite crystal structure was confirmed by XRD characterization. From our results, 1-D structure ZnO was grown along z-axis under all experimental conditions, but its crystallinity and aspect ratio were affected by the shape of precursor boat. By using the precursor oxidization protection method, formation of oxide layer before evaporation was inhibited, resulting in higher and constant Zn vapor supply throughout the reaction process. The synthesis process of high aspect ratio 1-D ZnO under the lower temperature has been developed by this method successfully. In conclusion, the 1-D, highly ordered, and vertically aligned ZnO nanostructures were synthesized on FTO. Since ZnO can be used for optoelectronics (i.e. solar cells), the 1-D ZnO synthesized by our method has potential to improve the performance of DSSCs.

Acknowledgement

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