# ZnS nanowires MOCVD preparation and characterization

J. M. Juárez G.*, V. Garibay** F. Juárez L.*

*Instituto Politécnico Nacional IPN-CIITEC,
Cerrada de Cecati S/N, México D. F. C. P. 02250, fjuarezl@ipn.mx
** Instituto Mexicano del Petróleo IMP.
Eje Central Lázaro Cárdenas Norte 152, México D.F. 07730, vgaribay@imp.mx

## ABSTRACT

An original MOCVD reactor was developed to grow zinc sulphide nanowires. The design of a heater system to have an improved control of the process and to obtain homogene deposition was performed. ZnS nanowires were successfully synthesized by simple metal-organic chemical vapor deposition technique from ZnS powders onto silicon substrates [111]. Substrates were carried out to a process of cleaning and impregnated with gold clusters from a colloidal solution. Scanning electron microscopy (SEM) observations show that the ZnS nanowires have diameters about 10-20 nm and lengths up to several micrometers. Atomic force microscopy (AFM) measurements were made in tapping mode using a silicon cantilever on digital Instruments Nanoscope.

***Keywords***: ZnS, MOCVD, nanowires.

## INTRODUCTION

Various ZnS nanostructured materials have been reported: nanoparticles (1), nanowires (2–4), nano ribbons (5–7), and nanotubes (8). Among them ZnS nanowires with high aspect ratio may become one of the prominent candidates in optoelectronic applications, ranging from telecommunication to medical therapeutics as a single-mode optical wave guide and ultra-violet (UV) nanoscale laser using the natural cavity. In recent years, considerable efforts have been made to synthesis of low dimensional ZnS materials and study of their physical properties, which are different from those of bulk crystals. A straight and smooth morphology is very important for the nanowires to be used in optoelectronic applications. Several synthesis methods of ZnS nanowires were reported such as the laser-assisted catalytic growth (LCG) method [9], the template method using gamma irradiation [10], the solution method containing an anionic surfactant [11] and thermal evaporation [12]. However, ZnS nanowires synthesized by previously reported solution methods were usually sphalerite, which is a low-temperature phase. In practical applications, single crystalline wurtzite ZnS is often needed. To synthesize single crystalline wurtzite ZnS nanowires, it is required to use expensive instruments with carrying out at high temperature.

In this communication MOCVD reactor was developed to grow zinc sulphide nanowires, we report a facile solution route to synthesize single crystalline wurtzite ZnS nanowires at temperature 500 °C. Observations on the microstructure of the as-synthesized ZnS by field emission scanning electron microscopy (FESEM) and X-ray diffraction (XRD) show a high quality in the single crystal. Wurzite ZnS nanowires were grown on silicon [111] substrate. In order gold cluster deposition was used to promote the growth of zinc sulphide. ZnS nanowires present morphology and structure columnar of size diameter from 30 to 100 nm. Atomic force microscopy (AFM) measurements were made in tapping mode using a silicon cantilever on digital Instruments Nanoscope. Optical properties of as-prepared ZnS nanowires were also investigated by measuring photoluminescence (PL) spectra and a strong ultra-violet (UV) emission near 560 nm was found.

## 1 EXPERIMENTAL

An original MOCVD reactor was developed to grow nanowires of zinc sulphide. The design of a heater system to have an improved control of the process and to obtain homogenous deposition was performed. Zinc sulphide nanowires were grown on silicon [111] substrate. In order gold cluster deposition was used to promote the growth of zinc sulphide. Co-reaction of dimethylzinc and $H_2S$ was used to grow ZnS to low temperature.

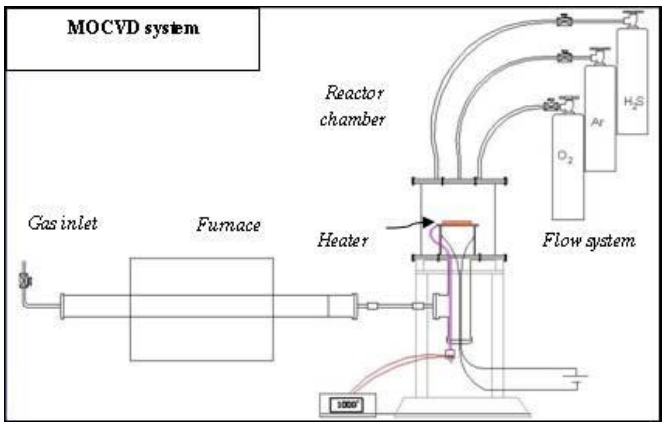


Figure 1. MOCVD system to grown ZnS nanowires.

All substrates were cleaned into an ultrasonic device using distilled water, acetone, distilled water and isopropyl alcohol and, dried with nitrogen gas. One face of substrates were etched with HF 1 mol and dried with nitrogen, cleaned with water and dried again. This last surface was impregnate of poly-Lysine and dried with nitrogen. After that a drop of gold colloids (20 nm diameter) was deposited on the surface of every substrate and dried at environment temperature.

A vertical tube chamber was used for the synthesis. An original heater was put into chamber. This heater achieves a strain control over substrate temperature. Zn(TMHD)2 was used as precursor for Zn metallic and $H_2S$ for sulfur gas source. Ar gas of high-purity was carried through the tube to cleaning of MOCVD system. The flow rate and pressure inside of chamber were kept at 50 sccm and 20 psi for all experiments. The heater was then heated at a rate of 50 °C/min to 500 °C and held at that temperature for 60 min.

## 2 RESULT AND DISCUSSION

The nanowires were characterized with FESEM, X-ray diffraction (XRD). Figure 2 show the morphology, size and elemental composition of the nanowires obtained.

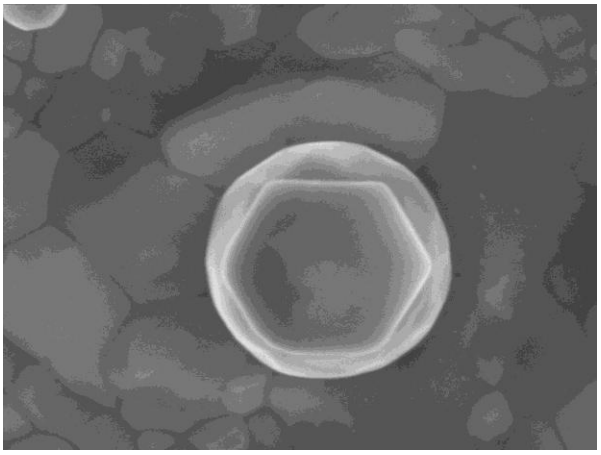

Figure 2. Morphology and size of ZnS nanowires obtained by FESEM.

SEM micrographs show a ZnS nanowires structure pretty column, this structure is formed by like hexagonal structure. This last support the results by DRX, where it shows a crystallite wurzite structure.

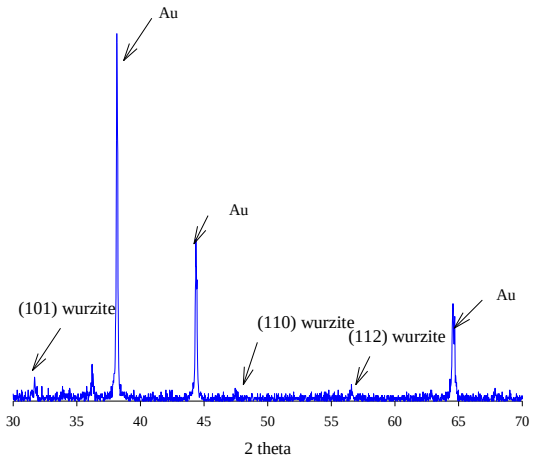


Figure 3. DRX of ZnS nanowires, wurzite structure is showed.

The surface morphology of typical ZnS nanowires is shown in Figure 4. The inset shows a plane view depicting the hillocks associated with different wires. The root mean-square (rms) roughness of these hillocks was found to be 500 nm. The hillocks representing the tops of the columnar wires are ~ 100 nm in diameter. The grains visible to AFM may be coalesced wires of smaller dimension, but future works TEM are needed to get a clearer picture.

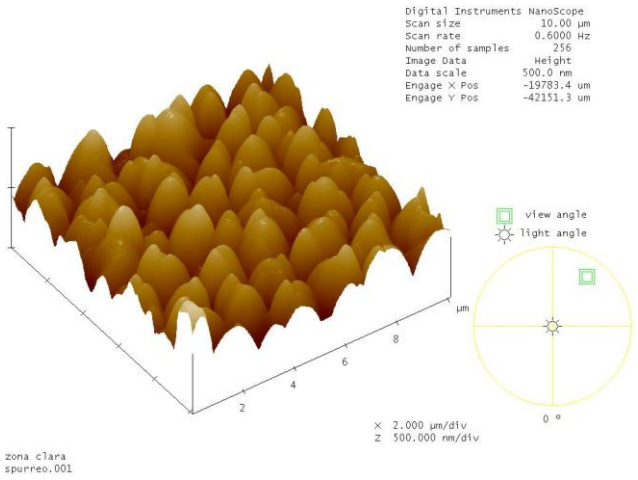


Figure 4. AFM image of ZnS nanowires grown on Silice (110).

Figure 5. In our experiment, Au clusters are served as catalyst and reacted with ZnS vapor to form Au-ZnS Alloy. When Au ions are doped in ZnS nanowires, the luminescence centers are formed. Because luminescence center maybe trapped electrons and holes, the luminescence peaks are long and broad [2]. Therefore, we can say that the

green-red light emission from the ZnS nanowires in our work could be attributed to the presence of Au ions.

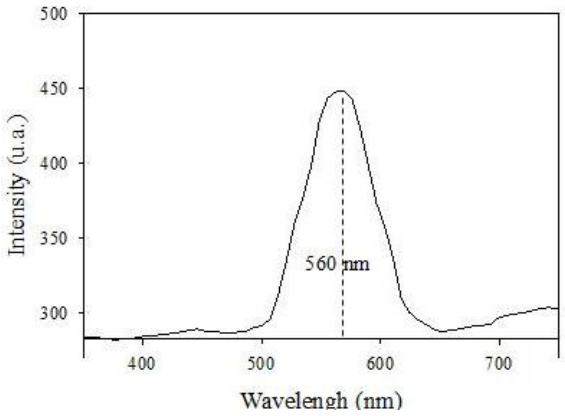


Figure 4. PL spectrum of synthesized ZnS nanowires at 560 nm.

## 3 CONCLUSIONS

An MOCVD system has been proposed as a very functional simple reactor. This work presents the first step of the growth of nanomaterials by MOCVD. As an example, ZnS nanowires have been synthesized in bulk quantities by the MOCVD process. FESEM observations show that the ZnS nanowires have diameters of about 30-100 nm and lengths of several micrometers. PL measurements taken on the bulk nanowires show green and red light emissions attributed to the presence of Au ions. In future work we will try to demonstrate that ZnS nanowires exhibit excellent optical and optoelectronic performance as well as strong UV emission.

## Acknowledgments

The authors are grateful for the support to conduct this work to COFAA, EDI-IPN and CONACYT. They are also indebted to CENAM for the facilities.

## REFERENCES

[1] Bohua Dong, Lixin Cao, Ge Su, Wei Liu, Hua Qu and Hui Zhai, Journal of Alloys and Compounds, 19 (2009).

[2] Hongxia Chen, Daning Shi, Jingshan Qi, Jianming Jia and Baolin Wang, Physics Letters A, **373**, Issue 3, 12 (2009), 371-375.

[3] Zhanqiang Deng, Junjie Qi, Yue Zhang, Qingliang Liao, Yunhua Huang and Jiawei Cao, Acta Physico-Chimica Sinica, **24,** Issue 2, (2008) 193-196.

[4] Hongxia Chen, Daning Shi, Jingshan Qi, and Baolin Wang, Physica E: Low-dimensional Systems and Nanostructures, **42**, Issue 1, (2009) 32-37.

[5] Soumitra Kar and Subhadra Chaudhuri , Chemical Physics Letters, **414**, Issues 1-3, 3 (2005) 40-46.

[6] Wen Yu, Pengfei Fang and Shaojie Wang, Applied Surface Science, **255**, Issue 11, 15 (2009), 5709-5713.

[7] Xiao Wu, KunWei Li and Hao Wang , Journal of Hazardous Materials, **174**, Issues 1-3, 15 (2010) 573-58.

[8] Ran Yi, Guanzhou Qiu and Xiaohe Liu, Journal of Solid State Chemistry, **182**, Issue 10, (2009) 2791-2795.

[9] N. Wang, Y. Cai and R.Q. Zhang, Materials Science and Engineering: R: Reports, **60**, Issues 1-6, 31 (2008) Pages 1-51.

[10] Xuan Xue, Jiafu Chen and Yong Hu Materials Letters, **61**, Issue 1, (2007) Pages 115-118.

[11] Lihong Dong, Ying Chu, Yanping Zhang, Yang Liu and Fuyong Yang Journal of Colloid and Interface Science, **308**, Issue 1, 1 (2007) 258-264.

[12] Heesung Moon, Changhun Nam, Changwook Kim and Bongsoo Kim. Materials Research Bulletin, **41**, Issue 11, 9 (2006) 2013-2017.