

Available online at www.sciencedirect.com**SciVerse ScienceDirect**

Physics Procedia 25 (2012) 278 – 286

Physics

Procedia

International Conference on Solid State Devices and Materials Science

MOCVD Growth of ZnO Nanowires Through Colloidal and Sputtered Au Seed Via Zn[TMHD]₂ Precursor

J. M. Juárez G.^a, J. Andraca A.^b, R. Cuenca A.^a, D. Jaramillo V.^a, F. Juárez L.^{a*}^a*Instituto Politécnico Nacional-CITEC, Cerrada de Cecati S/N, D.F. 02250, México.*^b*Instituto Politécnico Nacional-CNMN Luis Enrique Erro s/n UALM D.F. 07738, México.*

Abstract

Zinc oxide (ZnO) nanowire (NW) arrays were grown on Si (100) substrate by metal-organic chemical vapor deposition (MOCVD) via Zn[TMHD]₂ as precursor. Here we adopted two different procedures to grow ZnO NWs namely, colloid and sputtered Au pre-deposition on Si (100) substrate. Comparative studies based on the morphology and growth behavior of ZnO NWs were performed. The grown ZnO NWs were characterized by field-emission scanning electron microscopy (FE-SEM), Atomic Force Microscopy (AFM), Co-focal laser scanning microscopy (CLSM), and Raman spectroscopy.

© 2012 Published by Elsevier B.V. Selection and/or peer-review under responsibility of Garry Lee

Open access under [CC BY-NC-ND license](http://creativecommons.org/licenses/by-nc-nd/4.0/).

Keywords: Nanowires; MOCVD; colloidal-solution; Zinc Oxide; Zn[TMHD]₂

1. Introduction

Nanotubes, nanorods, and nanowires (NWs) of various semi-conductor materials have drawn much attention in recent years due to their novel physical properties and new promising application in nanodevices [1–4]. A one-dimensional (1D) structure has been demonstrated to be a promising building block in high electron mobility transistors [5], solar cells [6], and biosensors [7]. Among them, ZnO NWs are of great interest due to their wide band-gap, which allows the possibility to tune the optoelectronic devices working from infrared to ultraviolet range. Alignment with high optical quality NW configuration would potentially offer higher performance in nanodevices [8–11]. The high surface-to-volume ratio of

* Corresponding author. Tel.: +52 5 729 6000; fax: +52 5 561 7536.
E-mail address: fjuarezl@ipn.mx.

NWs makes the material properties of NWs extremely sensitive to the diameter. Reducing the NW diameter is an important issue for applications with controllable device performance [12–20]. Various methods have been developed for controlling the NW diameter, which include electron beam lithography (EBL), porous alumina membrane, photolithography, and etching process [21–25].

Alternatives techniques to synthesis of NWs implicate chemical vapour deposition using both halide and metalorganic precursor, and metal catalysis growth via the vapor – solid – liquid (VLS) mechanism [26–30]. According to the VLS growth mechanism, a small eutectic particle acts as a catalyst for decomposing and dissolving the gas phase reaction species, and after super saturation, it precipitates out the precursors to assist NW growth at a lower temperature [31]. The catalyst –assisted ZnO NW growth method is still the most widely exploited approach. On the other hand, some groups have reported the ZnS NWs growth without external catalyst [32–34]. Nevertheless, for commercial device application in the future, fabrication of well-ordered nanostructures with high density is very important because they can be effectually incorporated into devices. In the synthesis of semiconductors NWs, the control of the diameter size is very important, otherwise, if the scale of the materials is much larger than the Bohr radius, the materials will behave similar to the bulk materials, and no quantum confinement effects can be expected [35]. To investigate what controls the NWs growth direction, the information about the NW nucleation is necessary. Therefore, preparation of ZnO NWs array with high alignment has been attracting considerable interest, and various approaches have been developed.

In addition, the well-defined Au colloids could be exploited as catalysts for the growth of ZnO NWs with diameter distributions defined by the droplet catalysts. How to grow uniform, well controlled, and perfectly aligned NW arrays from desired materials is the ultimate goal of NW synthesis. However, in reality, the size of NWs may not be always determined by the size of catalyst. Diffusion kinetics and thermodynamic equilibrium may not be sufficient to predict all the NW epitaxial growth phenomena, such as the automatic formation of a buffer layer beneath NW arrays under certain circumstance.

The present study focuses on both sputtered and colloid Au seed particle and the vapor–liquid–solid (VLS) growth mechanism to performer the ZnO NWs growth by metal organic chemical vapour deposition (MOCVD) on the silicon [100] substrate. MOCVD conditions were determined into a reactor to decomposition of Bis(2,2,6,6-tetramethyl-3,5-heptanedionato)zinc II (Zn [TMHD]_2) precursor at priori not yet exploited to grow ZnO nanowires. The design of a heating system to obtain an improved control of the process and to obtain homogenous deposition is presented. Silicon (100) substrates were carried out to a process of cleaning and impregnated with gold seed separate from a colloidal-solution and sputtering process. ZnO nanowires were successfully growth by simple MOCVD technique from ZnO precursor. Field emission scanning electron microscope (FESEM) (JEOL Joel-JSM 6700F) was employed for examination of the morphology and microstructure of grown structures via both sputtered and colloid gold seed. X ray diffraction (XRD) was used to analysis the nanowires crystallinity. Atomic Force Microscopy (AFM) was used for analysis root-mean-square (MRS) surface. Micro-Raman and Confocal Laser Scanning Microscopy (CLSM) measurements were carried out to explore wavelength emission of the nanowires.

2. Experimental

2.1. Seed preparation

Steps by steps all Si (100) substrates were carried out a procedure of cleaning at priori before to depot Au seed; ultrasonically cleaning with acetone and de-ionized water for 5 minutes. After cleaning into isopropyl alcohol by 3 minutes, drying and chemical etching of substrate surface with HF 1 M. To follow of permeated at Poly-lysine in a beaker and drying with N_2 . Finally, gold (Au) seed was deposited in

separated substrates by sputtering and colloidal solution deposition (nanoparticle size ~20 nm Sigma Aldrich).

2.2. Growth ZnO nanowires

An in-house designed metal-organic chemical vapor deposition reactor was used for the growth of ZnO nanowires. The Silicon substrates with Au seed deposited were placed into a Hot – wall vertical reactor by means of a ceramic heater. In order to avoid a considerable temperature gradient this ceramic heater allows elevate the temperature raises promptly. The schematic of the experimental setup is shown in Fig. 1.

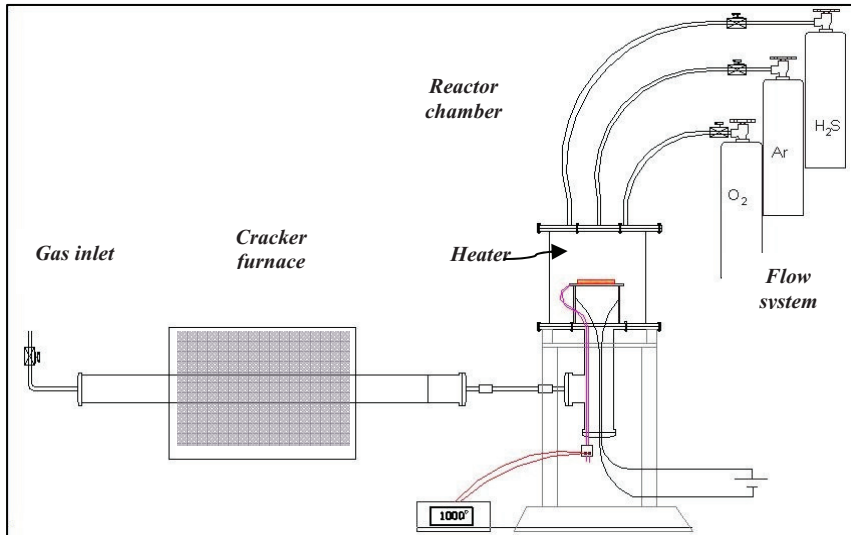


Fig. 1. Schematic MOCVD reactor design to grow ZnO nanowires.

All gases used in this setup are degree Laboratory Ar, O₂ and Zn[TMHD]₂ as precursor of Zn. This reactor was backfilled with flowing argon to atmospheric pressure. The substrates were then heated in flowing argon (30 sccm) to temperature 900 °C and work pressure of 760 Torr. Zn[TMHD]₂ was then introduced to reactor at sublimation temperature of 144 °C with flows of 30 sccm until forming a saturate atmosphere in Zn, 15 minutes later immediately was mixed with O₂. These temperatures were enough to transport the precursor until the zone reaction and free Zn[TMHD]₂ catalysis to deposit Zn co-reaction with O⁺.

3. Results and Discussions

SEM images of both colloidal and sputtered Au seeds on Silicon substrate were taken to analysis the initials morphological features, Fig. 2. The images revealed that both solution-colloidal and sputtering Au seed (Fig.2a 2b) were almost uniformly distributed on the Si surface.

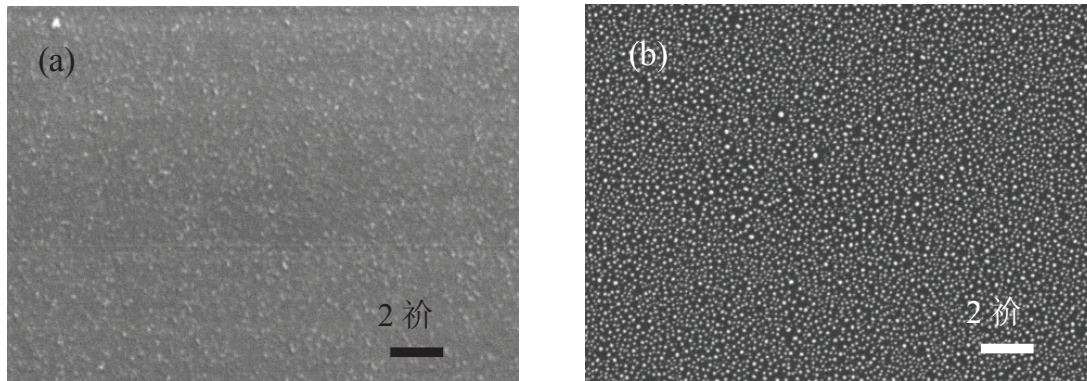


Fig. 2. SEM images of both Au seed colloidal-solution (a) and sputtering (b).

Fig. 3a shows the FESEM image of the nanowires structure after MOCVD growth conditions. FESEM observations show that the nanowires have diameters of about 100 nm and lengths of several nanometers. It can be seen from micrograph that the nanowires grown presents crystal forming structures like hexagonal form and also here at the tip nanowires can be seen the formation of structures like round ball, maybe with chemical composition in gold. This later is support by XRD results.

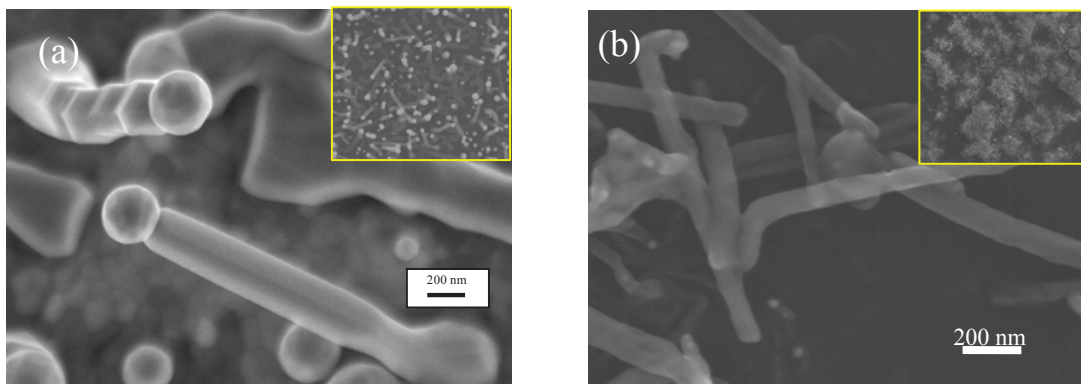


Fig. 3. FE-SEM images of the Zn nanowires growth via MOCVD: Au seed sputtered (a) and Au seed colloid (b).

In other hand the nanowires grown via colloidal Au seed shows a structure like hair, Fig. 3b. Nevertheless, these nanowires have diameters smaller of about 30 nm and lengths of several nanometers. Again, at the tip of the wires presents the formation of small Au crystallite.

The Fig. 4 shows the X-ray diffraction pattern of nanowires grown through Au seed sputtered (at the top) and Au seed colloidal (at the bottom) respectively. Both grazing angle patterns confirm that reflected peaks with preferred orientations can be indexed as ZnO structure crystal hexagonal (Zincite) close to ICSD Pattern 01-071-6424. The intensity of Au peaks was higher that ZnO reflected peaks maybe due to the position in the nanowire's tip. Since (1 0 0) face is one of the most stable faces in ZnO crystal with the lowest surface energy, most of these nanowires would grow along [1 0 1] direction normal to the (1 0 0) planes. The substrate temperature determines the saturation ratio of ZnO and two competitive growth

directions. Higher temperature ($>900\text{ }^{\circ}\text{C}$) prompts the growth along $[1\ 1\ 0]$ direction [36], while relatively lower temperature around $700\text{--}800\text{ }^{\circ}\text{C}$ benefits the growth along the $[2\ 1\ 0]$ direction.

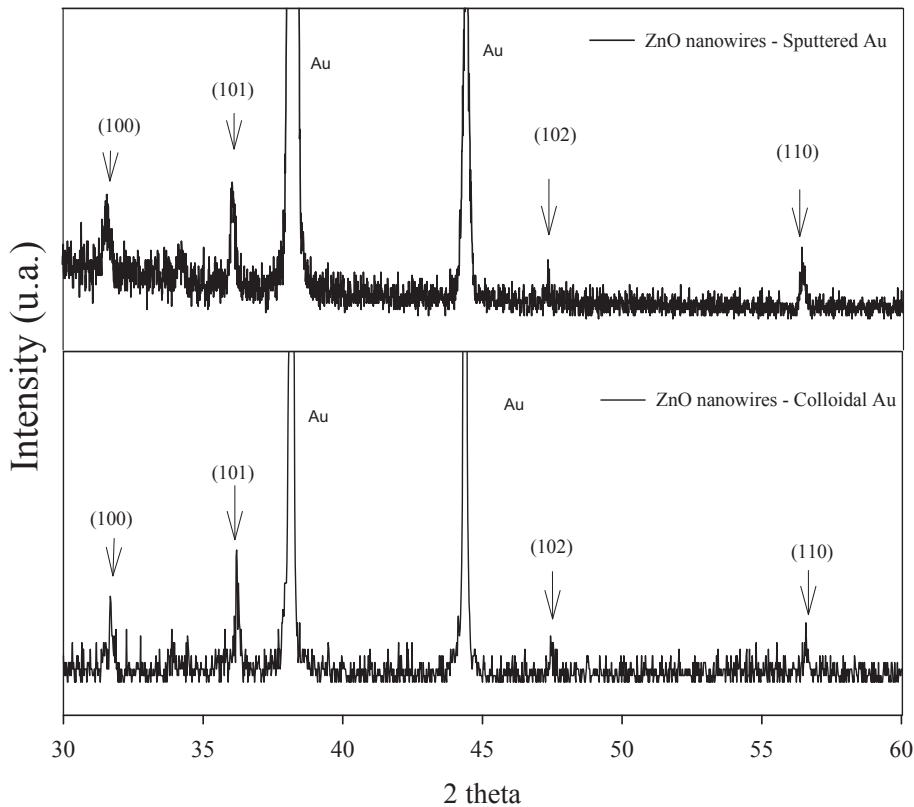


Fig. 4. X-ray diffraction images of the Zn nanowires growth by MOCVD starting from Au seed: sputtered (top) and colloid (below).

AFM images Fig. 5 shows the surface morphology of the NWs grown via Au colloidal and sputtered respectively. Au seed sputtered growth shows (Fig. 5b), typical three-dimensional (3D) columnar grains completely cover the whole surface and RMS surface roughness is as large as 500 nm. It suggests that the ZnO growth using Au seed sputtered undergoes a typical 3D growth mode, in which case, the inhomogeneous strain is fully relaxed. In contrast, nanowires grown through Au seed colloidal (Fig. 5(a)) shows an unexciting coalescent surface and its surface roughness decreased greatly to 4.18 nm.

The samples elaborated from Au seed sputtered are dense layers and consist in large crystallites elongated along three preferential directions roughly oriented at 120° from each others. These preferential orientations could possibly reflect the ZnO hexagonal symmetry to underlying substrate surface. Another explanation could imply both a strong anisotropy in the growth rate and a low nucleation rate at the substrate surface. Samples from colloidal Au seed the nanowires are less clear and smooth then the 3D growth of large misoriented crystallites may be result in very perturbed surfaces.

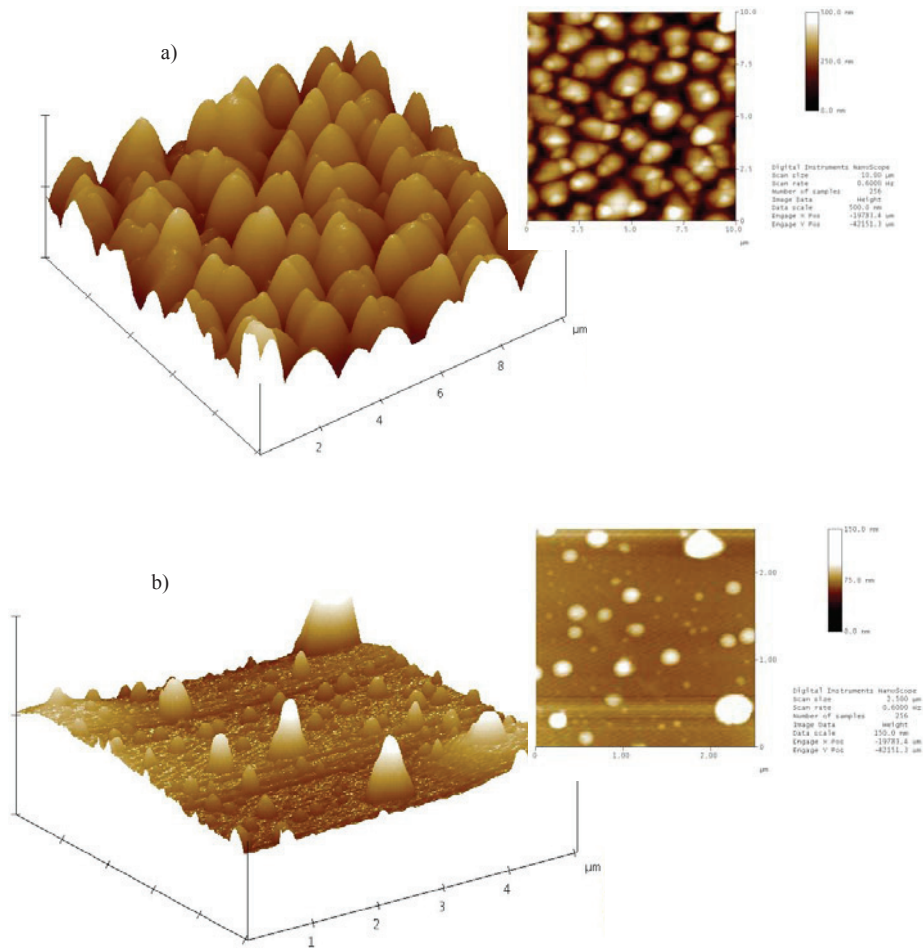


Fig. 5. AFM images of the ZnO nanowires growth by MOCVD starting from Au seed: sputtered (a) colloid (b).

The morphology of the wires is closely associated to the growth temperature and thus to the crystalline properties of the Au seed. Typical AFM images show that samples elaborated with colloidal are not homogenous structures but consist of large nanowires as seen in SEM micrographs. The micrograph corresponding to a typical sample grown presented in Fig. 3a in order to present more clearly the morphological features of interest. The wires present a columnar shaped morphology which strongly suggests that the growth is essentially columnar by nature. These columns are very uniform in size and height and particular orientation could be detected in their spatial distribution.

MicroRaman spectra obtained from the ZnO nanowires is shown in Fig. 6. Despite of presence of Au at the tip of the nanowires, the spectrum of ZnO is dominated by the wavelength peak (519 nm) from 295 nm source excitation. Here it is possible suggest a correlation between that Micro-raman emission at room temperature with confocal laser scanning microscopy images where find emission wavelength is evaluated in Fig. 7. Confocal laser scanning microscopy (CLSM or LSCM) is a technique for obtaining high-resolution optical images with depth selectivity.

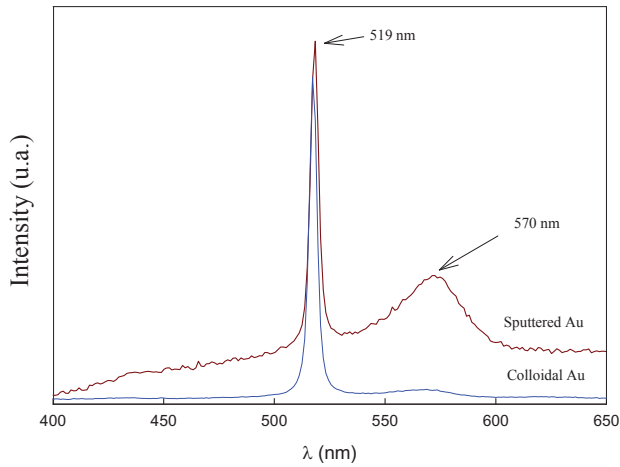


Fig. 6. Micro Raman from 295 nm excitation of the ZnO nanowires growth by MOCVD starting Au seed: colloidal and sputtered.

CLSM images revealed an emission wavelength from ZnO nanowires, Fig. 7a and b. It is clearly seen that in the case of growth through seed colloidal (a), the emission wavelength is higher in the green color. Indeed also is an interest show that CLSM images of grouped nanowires to hold a correlation with SEM images (Fig. 3b inset). In other side, it is not clear emission wavelength from ZnO nanowires grown via sputtered Au seed, may be due to that microscopy acquires in focus images from selected depths of the morphology of the nanowires, this known as optical sectioning of resulting image pixel corresponds to the relative intensity of detected light.

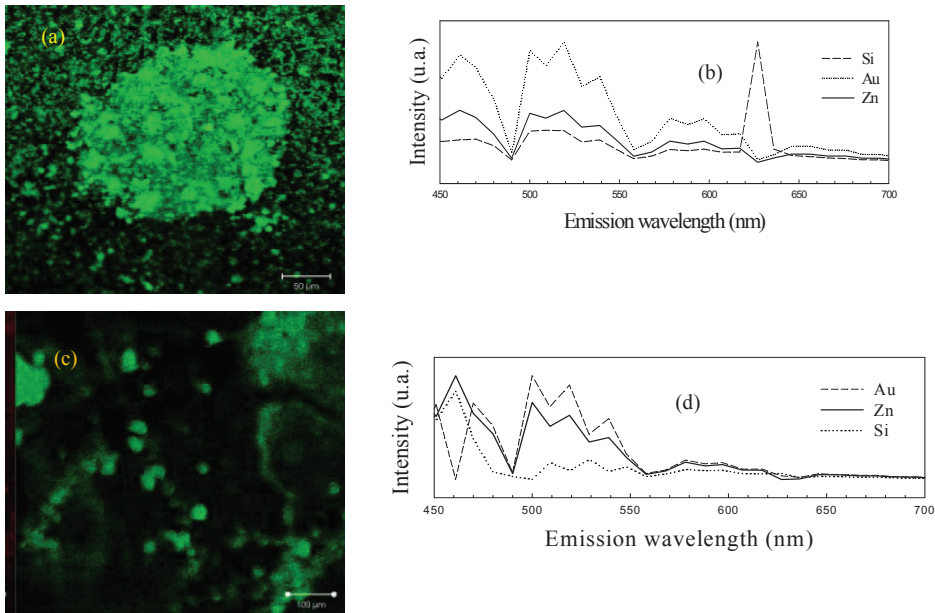


Fig. 7. CLSM images of the Zn nanowires growth by MOCVD starting from Au seed: colloid (a) sputtered (b).

The key feature of confocal microscopy is its ability to acquire in-focus images from selected depths, a process known as optical sectioning. Images are acquired point-by-point and reconstructed with a computer, allowing three-dimensional reconstructions of topologically complex objects. Finally, closed graph (fig 7(b) (d)) shows measurements of emission wavelength for Au, ZnO and Si, unfortunately all emission from these elements are closed, but emission peaks from ZnO are found at 519 and 600 nm

The micrographs images shown in Fig. 2a y b (sputtered and colloidal seed) revealed regular shaped structures with average size of 100-300 nm. Perhaps, various distinct stages can be suggested during Au seed sputtered structural evolution of the ZnO nanowires growth: The size of the Au seed deposited by sputtering is around 200 nm. Fig. 2a shows uniform and smooth distribution of Au seed on Si substrate before MOCVD process. After growing at 900 °C, the Au seed aggregates forms small flat with an average diameter of 300 nm (Fig. 3b). This is maybe due to the liquid-like mobility of Au atoms at high temperature. From SEM image, these particles are two times larger than those of pure Au islands, suggesting that ZnO and Au form an alloy with increased volume. It is suggested that as an increase of the growth duration of ZnO nanowires the formation of Au/ZnO mix is observed. The use of higher vapor pressure readily supersaturates the molten liquid with ZnO, and subsequent the recrystallization of ZnO nanowire from the saturated melt occurs [37].

Similar morphology like spheres at the tips of the nanowires is maybe responsible of both VLS and VSS mechanism that can co-exist into Au seed. From SEM micrographs shows nanowires structure, like-spheres at the tips of the nanowires formed to enhance the theory that VSS coexist with a VLS growth mechanism. Nucleation is kinetically hindered on the substrate and wire side facets, but the particle-wire interfaces acts as an unwell.

From classical nucleation theory to explain that heterogeneous nucleation of ice from water droplets on solid particles occurs at much higher rate at the three phase line between liquid water solid water and water vapour (crystal nucleation). Nebol's [38] considers the change in surface energies of the particle and wire that occur when nucleation occurs at the three phase boundary. There is an increase in the surface Gibbs free energy when the liquid particle is displaced by formation of a solid nucleus for a given range of particle-wire contact angles [39] similar approach emphasizing the energy gain that can be expected when a nucleus is formed at the edge of the particle-wire interface.

Henceforth work is oriented to developing a consistent model that can describe, and perhaps predict, the growth of nanowires of various materials from foreign –material particle in a variety of growth system.

4. Conclusion

An MOCVD system has been proposed as a very functional simple reactor. This work presents the first steps of the grown of ZnO nanowires by MOCVD through decomposition of Zn[TMHD]₂ as precursor of Zn. These nanowires have been grown through two kind gold seed allowed a characteristic growth of the ZnO wires. FESEM observations show that both kind ZnO nanowires have diameters in range 30-100 nm and lengths of several micrometers. However, similar chemical composition and morphology features were found. Confocal Laser Scanning Microscopy measurements on the bulk nanowires show green and red light emissions attributed to the presence of ZnO and gold ions respectively.

In future work we will to present the optical properties of ZnO nanowires 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.

Reference

- [1]Y. Xia, P. Yang, Y. Sun, Y. Wu, B. Mayers, B. Gates, Y. Yin, F. Kim, H. Yan, *Adv. Mater.* 15 (2003) 353-389.
- [2]Z. L. Wang, *Nanowires and Nanobelts-Materials, Properties and Devices*, Kluwer, Dordrecht/Plenum, Dordrecht, 2003.
- [3]V. G. Dubrovskii, G. E. Cirilin, V. M. Ustinov, *Semiconductors* 43 (2009) 1539-1584.
- [4]S. V. N. T. Kuchibhatla, A. S. Karakoti, D. Bera, S. Seal, *Prog. Mater. Sci.* 52 (2007) 699-913.
- [5]Y. Li, J. Xiang, F. Qian, S. Gradecak, Y. Fang, Y. Wu, H. Yang, D. A. Blom, C. M. Lieber, *Nano Lett.* 6 (2006) 1468-1473.
- [6]M. Law, L. E. Greene, J. C. Johnson, R. Saykally, P. Yang, *Nature Mater.* 4 (2005) 455-459.
- [7]G. Zheng, F. Patolsky, Y. Cui, W.U. Wang, C. M. Lieber, *Nat. Biotechnol.* 23 (2005) 1294-1301.
- [8]R. Calarco, M. Marso, T. Richter, A. I. Aykanat, R. Meijers, A.V.D. Hart, T. Stoica, H. Luth, *Nano Lett.* 5 (2005) 981-984.
- [9]A. A. Talin, F. Leonard, B. S. Swartzentruber, X. Wang, S. D. Hersee, *Phys. Rev. Lett.* 101 (2008) 076802-01.
- [10]A. Cavallini, L. Polenta, M. Rossi, T. Stoica, R. Calarco, R. J. Meijers, T. Richter, H. Luth, *Nano Lett.* 7 (2007) 2166-2170.
- [11]E.O.S. Nolte, T. Stoica, T. Gotschke, F. Limbach, E. Sutter, P. Sutter, R. Calarco, *Appl. Phys. Lett.* 96 (2010) 091907.
- [12]S. Ishizawa, K. Sekiguchi, A. Kikuchi, K. Kishino, *Phys. Status Solidi B* 244 (2007) 1815-1819.
- [13]S. Ishizawa, K. Kishino, A. Kikuchi, *Appl. Phys. Exp.* 1 (2008) 015006.
- [14]K. Kishino, T. Hoshino, S. Ishizawa, A. Kikuchi, *Electron. Lett.* 44 (2008) 819-821
- [15]H. Sekiguchi, K. Kishino, A. Kikuchi, *Appl. Phys. Exp.* 1 (2008) 124002.
- [16]K. Kishino, H. Sekiguchi, A. Kikuchi, *J. Cryst. Growth* 311 (2009) 2063-2068.
- [17]T. Kouno, K. Kishino, K. Yamano, A. Kikuchi, *Opt. Exp.* 17 (2009) 20440-20447.
- [18]K. A. Bertness, A. W. Sanders, D. M. Rourke, T. E. Harvey, A. Roshko, J. B. Schlager, N. A. Sanford, *Adv. Funct. Mater.* 20 (2010) 2911-2915.
- [19]W. Xin, S. Xinyu, F. Michael, H. Stephen, *App. Phys. Lett.* 89 (2006) 233115.
- [20]S. D. Hersee, X. Sun, X. Wang, *Nano Lett.* 6 (2006) 1808-1811.
- [21]B. S. Simpkins, P. E. Pehrsson, M. L. Taheri, R. M. Stroud, *J. Appl. Phys.* 101 (2007) 094305.
- [22]T. E. Bogart, S. Dey, K.K. Lew, S.E. Mohny, J. M. Redwing, *Adv. Mater.* 17 (2005) 114-117.
- [23]E. C. Greyson, Y. Babayan, T. W. Odom, *Adv. Mater.* 16 (2004) 1348-1352.
- [24]K.H. Lee, P.L. Lo, J.D. Liao, J.G. Chen, *J. Electrochem. Soc.* 157 (2010) K84.
- [25]M.E. Messing, K. Hillerich, J. Bolinsson, K. Storm, J. Johansson, K.A. Dick, K. Deppert, *Nano Res.* 3 (2010) 506-519.
- [26]T. Stoica, E. Sutter, R.J. Meijers, R.K. Debnath, R. Calarco, H. Luth, D. Gruzmacher, *Small* 4 (2008) 751-754.
- [27]G.T. Wang, A.A. Talin, D.J. Werder, J.R. Creighton, E. Lai, R.J. Anderson, I. Arslan, *Nanotechnology* 17 (2006) 5773.
- [28]S. Biswas, S. Kar, T. Choshal, V.D. Ashok, S. Chakrabarti, S. Chaudhuri, *Mater. Res. Bull.* 42 (2007) 428-436.
- [29]C.N.R. Rao, F.L. Deepak, G. Gundiah, A. Govindaraj, *Prog. Solid State Chem.* 31 (2003) 5-147.
- [30]E.S. Jang, Y. H. Ra, Y. M. Lee, S.H. Yun, D.W. Kim, R. Navamathavan, J.S. Kim, I.H. Lee, C.R. Lee, *Jpn. Appl. Phys.* 48 (2009) 091001.
- [31]R.S. Wagner, W.C. Ellis, *Appl. Phys. Lett.* 4 (1964) 89-90.
- [32]R. Songmuang, O. Landre, B. Daudin, *Appl. Phys. Lett.* 91 (2007) 251902.
- [33]B.S. Xu, L.Y. Zhai, J. Liang, S.F. Ma, H.S. Jia, X.G. Liu, *J. Cryst. Growth* 291 (2006) 34-39.
- [34]R. K. Debnath, R. Meijers, T. Tichter, T. Stoica, R. Calarco, H Luth, *Appl. Phys. Lett.* 90 (2007) 123117.
- [35]L. Cademartiri, G.A. Ozin, *Adv. Mater.* 21 (2009) 1013-1020.
- [36]Y. W. Wang, L.D. Zhang, C. H. Liang, G.Z. Wang, X.S. Peng, *Chem. Phys. Lett.* 357 (2002) 314-318.
- [37]A. Dick Kimberly, *Progress in Cryst. Growth and Charact. of Mat.*, 54 (2008) 138-173.
- [38]V.A. Nebol'sin, A.A. Shchetinin, *Inorg. Mater* 39 (2003) 899-903.
- [39]F. Glass, J.-C. Harmand, G. Patriarche, *Phys. Rev. Lett.* 99 (2007) 146101.