Hollow ZnO Nano-Cone Synthesis via Catalyst Free MOCVD

Wei Zhang[1], Karlheinz Strobl[1] and Yi Tu[1]
[1]CVD Equipment Corporation,
1860 Smithtown Avenue, Ronkonkoma, NY 11779

Applications Laboratory

ABSTRACT

Zinc oxide is a wide bandgap material with excellent semiconducting, photonic and piezoelectric properties. In the past ten years zinc oxide nano-structures such as nano-wires and nano-rods have received great interest due to their unique dimensional and material properties in the area of photonics, electronics, mechanics, energy recovery, etc. In this poster we report the manufacturing process of a new shape, i.e. hollow hexagonal ZnO nano-cones. We grew them on different kinds of substrate using a low pressure, catalyst free, metal organic chemical vapor deposition (MOCVD) process on a First Nano EasyTube™ 3000 MOCVD system. Nitrogen was used as carrier gas to bring the reactants, DEZ and H_2O, to the substrate surface. At the right balance of process temperature and carrier/precursor gas flow rate the ZnO nano-structure transitioned into a hollow hexagonal cone growth mode. The both one and two dimensional aspects of these catalyst free hollow hexagonal ZnO nano-cones, which are novel to the best of our knowledge, could lead to new applications in photonics, near field probing, chemical sensors, quantum confinement, electronic, etc.

EasyTube™ 3000 SYSTEM

- **EasyTube™ 3000** modular platform houses several key process components including a 3" diameter quartz process chamber, a computer controlled, fully automated process control system for maximum safety and process reproducibility, automatic sample loaders, pumps, an ultra high purity (UHP) gas and vapor delivery system and an EasyGas™ 610 exhaust gas treatment system - all for maximum system flexibility.
- **Three-Zone Furnace** with cascade control provides better temperature stability and uniformity over a large area. Internal thermocouples measure actual temperature over samples. Furnace lid opens automatically during cooling down stage to save operating time and improve productivity. This versatile system has been adjusted to deposit silicon nano-wire, silicon dioxide, SiC_xO_y, APCVD Fluorine doped ZnO and LPCVD Boron doped ZnO successfully. Temperature distribution was also numerically predicted inside the reaction process tube. Computation Fluid Dynamics (CFD) software, ANSYS FLUENT, is used to conduct the 3-D thermal modeling including conduction, convection and radiation. By applying controlled temperature profiles to the inner wall of the three-zone furnace, a highly uniform temperature distribution can be achieved on the substrate paddle as shown in the thermal model analysis graph shown below.

EasyTube™ 3000 System

Three-Zone Furnace

Temperature Profile in Furnace

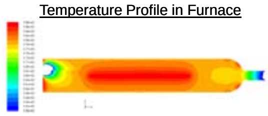
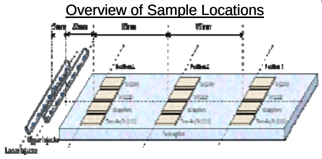


Figure 1. Easy Tube™ 3000 System

EXPERIMENT SETUP

Zinc Oxide hollow hexagonal nano-cones were deposited on Au coated Si (100), Sapphire, Si (100) and Si (111) substrates by low pressure, metal organic chemical vapor deposition (MOCVD) process on an EasyTube™ 3000 MOCVD system. Nitrogen was used as the carrier gas for diethyl zinc (DEZ), and DI water. Both vapors where delivered through a different injector and mixed right before reaching the substrate. Process parameters such as temperature and DEZ/H2O ratio has been varied for different types of substrates and locations from injectors to obtain these hollow ZnO nano-cones.

Overview of Sample Locations



- **Characterization**: Surface topography images have been taken by Scanning Electron Microscopy (SEM) to analyze the surface morphology of the ZnO nano-cones. Cross-section views were obtained by splitting the substrates to characterize the crystallographic orientation and the microstructure of these nano-cones.

Typical process conditions for hollow hexagonal ZnO nano-cones deposition

Process Tube		DEZ Bubbler			H_2O Bubbler			DEZ/H_2O Ratio
Temp.	Pressure	Temp.	Pressure	Carrier N_2	Temp.	Pressure	Carrier N_2	
[C]	[Torr]	[C]	[Torr]	[sccm]	[C]	[Torr]	[sccm]	[-]
575-750	0.6-2	20	300	10 to 40	30	200	80	0.5:19 to 2:19

RESULTS & DISCUSSION

Effect of Process Temperature on Growth Morphology

When we increased the process temperature from 500 ^{0}C to 625 ^{0}C gradually, the ZnO structure changed from a rough coating with multiple orientations (Fig. 2a) to hexagonal rods (Fig. 2b), to solid hexagonal nano-cones (Fig. 2c), and finally to hollow hexagonal nano-cones (Fig. 2d). Lower temperature results in higher ZnO super-saturation on the substrate, favoring the ZnO growth at all different orientations. Higher temperature reduces the super-saturation due to intensified gas phase reactions. At the same time the molecule surface energy is increased. Growth is therefore favored on the cone walls having a higher free energy.

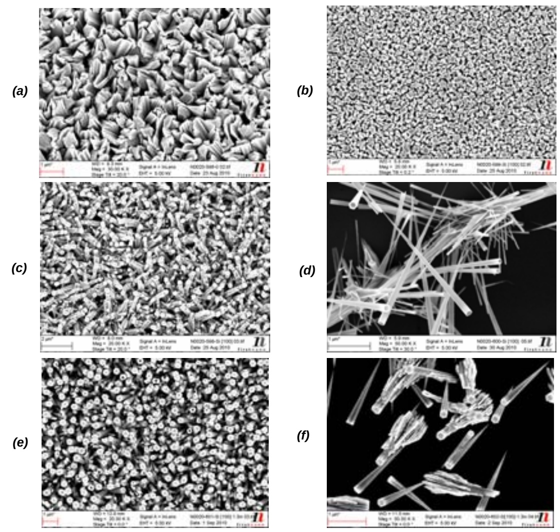


Figure 2. SEM for ZnO nano-structures at different process temperature and DEZ/H_2O ratio (a) 500℃, DEZ:H_2O=1:19, (b) 575℃, DEZ:H_2O=1:19, (c) 600℃, DEZ:H_2O=1:19, (d) 625℃, DEZ:H_2O=1:19, (e) 625℃, DEZ:H_2O=2:19, and (f) 625℃, DEZ:H_2O=0.5:19.

Influence of DEZ/H_2O ration on Hollow ZnO nano-cones

ZnO nano-structures with the ratio of DEZ:H_2O set at 1:19, 2:19, and 0.5:19 are shown in Figs. 2(d)-(f), respectively, for a Si (100) substrate with a 625 ^{0}C process temperature and chamber pressure of 600 mTorr. High quality hollow hexagonal ZnO nano-cones have been obtained with the DEZ:H_2O =1:19 ratio. Increasing this ratio changes the growth from hollow to solid nano-cones. Lowering the ratio reduces the growth rate significantly.

Influence of Substrate on Hollow ZnO nano-cones

For a growth temperature of 630 ^{0}C, a chamber pressure of 0.6 Torr, a H_2O/DEZ mole ratio of 1:19 and a growth time of 20 minutes we obtained high quality hollow hexagonal ZnO nano-cones on the three catalyst free substrates, as well as on the Si(100) substrate with Au catalyst, indicating that the growth is not substrate dependent.

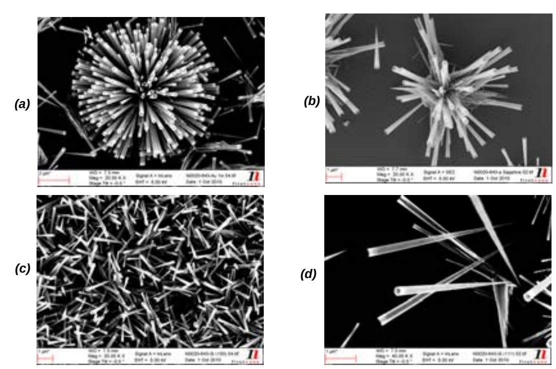


Figure 3. Top view of hollow ZnO nano-cones on different substrates (a) 5nm Au coated Si (111); (b) a Sapphire; (c) Si (100); and (d) Si (111).

CONCLUSIONS

In this poster, we reported the manufacturing process of a new nano-structure, i.e. catalyst free hollow hexagonal ZnO nano-cones on a First Nano EasyTube™ 3000 system. High quality hollow hexagonal ZnO nano-cones were successfully obtained at higher temperature between 625 ^{0}C to 635 ^{0}C. We believe that low ZnO super-saturation and high molecule surface energy have been satisfied at the same time in order to favor the growth on the six higher free energy cone walls. The effect of precursor ratio on the growth has also been analyzed and preliminary concluded that super-saturation is the key to the hollow ZnO nano-cone formation. Four different substrates with and without catalyst have been used to successfully grow hollow ZnO nano-cones. At the optimized process conditions hollow ZnO nano-cones were successfully synthesized on all the substrates. The catalyst free hollow ZnO nano-cones could have higher electrical and optical qualities since the diffusion of impurities from the catalyst is avoided and this novel 2D and 3D material form could lead to new optical and electrical effects.