SHAPE EVOLUTION IN ONE-DIMENSIONAL ZnO NANOSTRUCTURES GROWN FROM ZnO NANOPOWDER SOURCE: VAPOR–LIQUID–SOLID VERSUS VAPOR–SOLID GROWTH MECHANISMS

SOUMEN DHARA and P. K. GIRI*

Department of Physics
Indian Institute of Technology Guwahati
Guwahati-781 039, India
*giri@iitg.ernet.in

Here we report on the growth and evolution of ZnO nanowires grown from ZnO nanopowder as a source material using a horizontal muffle furnace. The shape evolution has been studied with variation in growth temperature and zinc vapor pressure. The structural analysis on these nanostructures shows c-axis oriented aligned growth. Scanning electron microscopy imaging of these nanostructures revealed the shape evolution from nanowires to nanoribbons and then to nanorods as the growth temperature increases from 650°C to 870°C. At 650°C, only vertical nanowires have been observed and with increase in growth temperature nanowires transform to nanoribbons and then to nanorods at 870°C. And we also observed simultaneous growth of nanorods and nanoribbons under a specific growth condition. We believe that these nanowires and nanorods were formed by vapor–liquid–solid growth mechanism (catalyst-mediated growth), whereas nanoribbons were grown by vapor–solid growth mechanism (without the aid of a metal catalyst). We observed simultaneous occurrence of vapor–liquid–solid and vapor–solid growth mechanisms at a particular growth temperature. These ZnO nanowires exhibit bound exciton related UV emission at ~ 379 nm, and defect-emission band in the visible region. Possible growth mechanism, shape evolution, and simultaneous growth of two types of one-dimensional ZnO nanostructures under the same growth condition are discussed.

Keywords: Nanostructures shape evolution; vapor–liquid–solid; vapor–solid growth.

1. Introduction

ZnO is an important material for its huge application prospects in different optoelectronic devices due to its wide direct band gap (3.37 eV) and large exciton binding energy, about 60 meV at room temperature.1 This high exciton binding energy enables the role of phonons at room temperature and emits strong excitonic emission at high temperature.2 Various compound semiconducting nanomaterials have been fabricated for use in optoelectronic devices. In particular, metal-oxide semiconductor such as ZnO has gained enormous significance for its rich varieties of nanostructures, excellent crystallinity, chemical stability, thermal stability, and wide band gap. Each nanostructure has specific applications in nanosize electronic, optical, and sensor devices.3–5

One-dimensional ZnO nanostructures have been extensively studied and usually grown by vapor–liquid–solid (VLS) mechanism using gold or copper as catalyst.6,7 Bulk zinc powder or zinc oxide powder has been extensively used for the growth of one-dimensional nanostructures of ZnO.6,8 Different groups have reported about the production of
varieties of ZnO nanostructures, including rods, wires, belts, ribbons, tetrapods, etc. with different arrangement of process parameters under different growth mechanisms. For successful incorporation to functional nanodevices, it is important to grow nanostructures with desired shape, size, and orientation. It is generally believed that source material, growth temperature, and vapor pressure concentration strongly controlled the final shape of the nanostructures. Ye et al. have studied morphology derivation of ZnO nanostructures from nanoplatelets to nanowires using bulk ZnO powder as a source material by vapor–solid (VS) growth process. In this paper, we report the growth and shape evolution of ZnO nanowires during VLS growth process using ZnO nanopowder as the source material. This shape evolution has been observed with variation in growth temperature and zinc vapor pressure.

2. Experimental Details

One-dimensional ZnO nanostructures were synthesized in a horizontal muffle furnace using a quartz tube by a vapor deposition method using gold catalyst. Commercial ZnO nanopowder (Sigma-Aldrich, purity 99.999%) was mixed with high-purity graphite powder (Fluka) in 1:1 weight ratio, and the mixture was used as source material for deposition. The mixture was placed at the center of the furnace inside the quartz tube. About 2 nm gold layer was deposited on the cleaned Si(100) substrate for catalyst-assisted growth and it was placed at different temperature zones of the furnace inside the quartz tube. Then, the temperature of the furnace was ramped to 950°C to start deposition and maintained for 30 min. Ar gas was used as vapor carrier gas with a flow rate of 70 sccm.

After deposition, shape and structural morphology of the grayish-black colored samples were analyzed using scanning electron microscopy (SEM, LEO 1430VP) and X-ray diffraction with Cu Kα radiation (XRD, Seifert 3003 T/T). Optical properties of these nanostructures were studied with excitation of 325 nm He–Cd laser using a fluorimeter (Edinburg, FS-920P).

3. Results and Discussion

3.1. ZnO nanostructures evolution

After deposition, varieties of one-dimensional ZnO nanostructures have been observed on gold-coated Si substrates. The shapes of the nanostructures changed from nanowires to nanoribbons and then to nanorods with decrease in the distances between the source material and substrate. The morphology of the nanostructures grown at 750°C is shown in Fig. 1(a), where dense nanowires were formed over areas extending to several square millimeters. These nanowires have diameter of few tens of nanometers and length about few microns. We also observed the formation of nanowires with similar morphology at growth temperature down to 650°C (not shown).

When the substrate is placed closer to the source material, i.e., at higher substrate temperature (850°C), morphology of the nanostructures changed to high density of long nanoribbons, which is shown in Fig. 1(b). The nanoribbons have length of >10 μm and width of several hundreds of nanometers.

![](image1)

Fig. 1. SEM images (tilted view) of various one-dimensional ZnO nanostructures grown at different temperatures: (a) vertical growth of nanowires, (b) long nanoribbons, (c) vertical nanorods and straight tapered nanoribbons, (d) dense nanorods.
We observed the tapered shaped nanoribbons with smallest tip size about 40 nm. In this temperature range, along with nanoribbons some nanorods may also have formed. But these nanorods are not visible in the image due to the long length and high density of the nanoribbons. Because ZnO nanoribbons and nanorods are generally formed in the temperature range of 800°C–1000°C, we observed the formation of nanorods at high temperature. And in this temperature range, the ribbons grow much faster compared to the rods. At 860°C substrate temperature, nanorods are formed along with some straight nanoribbons, as shown in Fig. 1(c). This image reveals that the nanorods were grown perpendicular to the Si substrate plane and have hexagonal facet. In this temperature region, nanoribbons and nanorods are simultaneously grown on the Si substrate with almost equal yield. Finally, at 870°C, which is nearer to the source material, dense nanorods were formed (Fig. 1(d)). The nanorods form an array nearly parallel to each other and perpendicular to the substrate plane. In this temperature region, mainly rods were formed with very few straight ribbons whose diameter is large. The nanorods diameter is about 200–300 nm and length of several microns. We observed temperature-dependent shape of ZnO nanostructure. At lower growth temperature and lower zinc vapor pressure, nanowires were formed and then transformed toward nanoribbons and then to nanorods at high temperature and high vapor pressure. First, we obtained nanowire growth at relatively low temperature (650°C) that reported for bulk ZnO sources. Second, using ZnO nanopowder source, we observed simultaneous formation of two types of nanostructures (ribbons and rods) at higher temperature, which was not observed using bulk ZnO powder as source.

XRD studies of these nanostructures show crystalline hexagonal wurtzite structure. Figures 2(a)–2(c) show XRD spectra of the nanowires, nanoribbons, and nanorods, respectively. The strong peak corresponding to ZnO (002) plane indicates nanostructures grown along the c-axis of ZnO, which is perpendicular to the substrate plane. The additional peak at 54.8° in Fig. 2(b) corresponds to graphite (222) plane, which is used in source mixture as a reducing agent. Sharp (002) peaks in Figs. 2(a) and 2(c) indicate well aligned growth of nanowires and nanorods, whereas nanoribbons do not show any preferential alignment. The XRD results are in agreement with the SEM results, which also show preferential vertically aligned growth.

![Fig. 1](Continued)

![Fig. 2](Continued)
3.2. **Formation mechanism**

Formation of varieties of ZnO nanostructures mainly depends on growth temperature, surface energy of the growth plane, and temperature of the source material and zinc vapor pressure. As high temperature region was nearer to the ZnO source, there was a large variation of zinc vapor pressure and concentration in different temperature regions. During the growth process, the above parameters strongly influence the final shape of the ZnO nanostructures.

Formation of ribbons and rods with different sizes at a particular growth condition can be explained by simultaneous occurrence of VLS and VS growth kinetics. Due to ultrathin gold layer, at high temperature zinc vapor can “see” bare silicon surface surrounding the gold droplets throughout the substrate. In the source material there was a large variation in ZnO nanoparticles' size (25–100 nm). During thermal evaporation, smaller size nanoparticles evaporate first compared to larger size particles, and then deposited on the gold droplets and surrounding bare Si substrate surface separately, which is placed nearer to the source. This deposition initiates the nanostructures growth by VLS process on the gold droplets, resulting in the growth of nanorods. On the other hand, zinc vapor deposited on the bare Si regions results in the growth of nanoribbons by the VS process. In VS mechanism, zinc vapor tends to diffuse toward the whole growth front, and in VLS, growth always takes place at the solid/liquid interface. This results in a slower growth rate VLS process compared to VS growth rate, yielding longer nanoribbons in VS growth process. Occurrence of simultaneous growth does not take place for growth at lower temperatures. There may be two possible reasons for this: (a) temperature below 800°C is not sufficient to grow ribbon structures; (b) when most of the nanoparticles vaporized at higher temperature, zinc vapor has higher concentration. During condensation, zinc vapor formed small vapor clouds, and preferential growth takes place by the catalytic process mediated by gold droplets.

3.3. **Optical properties**

Figure 3 shows room temperature photoluminescence (PL) spectra of ZnO: (a) nanorods, (b) nanowires, and (c) nanoribbons. ZnO nanowires exhibit strong near band edge (NBE) UV emission at 380 nm and broad green emission at 526 nm. Nanorods and nanoribbons show similar spectra with UV peak at ~379 nm and another peak at 500 nm in nanorods and 527 nm in nanoribbons, respectively. The NBE emission is due to bound excitonic recombination, and green emission is attributed due to the recombination of photogenerated holes with the electrons belonging to oxygen vacancy states on the surface. With increase in growth temperature, intensity ratio of UV to visible emission peak decreased. Therefore, it is possible that nanostructures grown at higher temperature have more oxygen vacancy states, yielding strong visible emission. The nanowires have the stronger UV emission intensity due to the enhanced recombination efficiency caused by confinement effect.

4. **Conclusions**

We observed temperature-dependent shape evolution of ZnO nanostructures as a function of growth temperature and effect of ZnO nanopowder source. At lower growth temperature (650°C) high-density nanowires were formed, and with increase in growth temperature nanoribbons and then nanorods were obtained finally at 870°C. So, nanowires and nanoribbons formation is favorable at lower temperature and lower vapor pressure region, and nanorods formation is favorable at higher temperature and higher vapor pressure. Due to the effect of large size distribution of ZnO nanoparticles and ultrathin gold layer on the Si substrate, we observed the formation of nanoribbons by VS process and nanorods by VLS process at the same growth temperature.
References
