

Growth of ZnO Nanorods on GaN using aqueous solution method

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Abstract— Uniformly distributed ZnO nanorods with diameter 80-120 nm and 1-2 μ m long have been successfully grown at low temperatures on GaN by using the inexpensive aqueous solution method. The formation of the ZnO nanorods and the growth parameters are controlled by reactant concentration, temperature and pH. No catalyst is required. The XRD studies show that the ZnO nanorods are single crystals and that they grow along the c axis of the crystal plane. The room temperature photoluminescence measurements have shown ultraviolet peaks at 388nm with high intensity, which are comparable to those found in high quality ZnO films. The mechanism of the nanorod growth in the aqueous solution is proposed. The dependence of the ZnO nanorods on the growth parameters was also investigated. While changing the growth temperature from 60^oC to 150^oC, the morphology of the ZnO nanorods changed from sharp tip with high aspect ratio to flat tip with smaller aspect ratio. These kinds of structure are useful in laser and field emission application

I. Introduction

Semiconductor nanostructure are promising candidates for future electronic and photonic devices. In nanostructure, the density of states of carrier is concentrated at some specific energy levels, which enable enhancement of exciton oscillator strength and light emitting efficiency. As a result, the performance of nanostructure based optical devices is expected to improve and to be less temperature dependent.

So far, many semiconducting materials have been grown into nanostructures such as nanowires and nanorods from Si¹, Ge², GaAs³, and GaN⁴. Nanostructures based on wide band gap semiconductors such as ZnO is of particular interest because of its novel properties such as large direct band gap (3.37eV), high exciton binding energy (60meV), and tunable band gap formed by alloying with CdO or MgO⁵. It is

a unique material which exhibits both semiconducting and piezoelectric properties. In addition, it is also a promising material for exciton based optoelectronic devices emitting in the UV region. As compared to GaN and SiC, ZnO exhibits higher quantum efficiency and the possibility of being wet etched, which makes ZnO an ideal candidate for optoelectronic devices.

Many deposition methods have been used to fabricate the ZnO such as metal organic chemical vapor deposition (MOCVD)⁶, pulse laser deposition⁷, radio frequency magnetron sputtering⁸, and anodized aluminum oxide membrane⁹. In this report, the ZnO nanorods were epitaxially grown by using the aqueous solution. This growth method showed some advantages compared with others, such as use of simple equipment, low temperature deposition (100^oC), low cost, less hazardous, and no need for use of metal catalysts. The GaN substrate was used as a template for the ZnO nanorod growth since these materials have the same wurtzite crystal structure, similar band gap energy (~3.7eV), and low lattice constant misfit (1.9%).

Growing ZnO nanorods on GaN offers a new method to fabricate the GaN nanotube since the ZnO is easily decomposed in the hydrogen ambient at 600^oC¹⁰. In addition, n-ZnO nanorod on p-GaN has a potential application in heterojunction based device¹¹ due to the increase in carrier injection efficiency in the nanojunction¹²⁻¹³. To the best of our knowledge, this is the first report on growth of ZnO nanorods on GaN using wet chemistry method.

II. Experiment

Well aligned ZnO nanorod arrays were grown directly on the GaN substrate. The experiment procedure was designed as follows: Zn (CH₃COO)₂ .2H₂O (0.016M) was first dissolved in deionized water at room temperature. Then, NH₄OH (0.095M) was added into the solution to create the alkaline environment (pH 10). The resulting suspension was transferred into a Teflon – lined stainless steel autoclave.

Next, the GaN substrate, after cleaning with deionized water, was dipped into the solution and suspended in the autoclave by a tantalum wire. Finally, the autoclave was sealed and put into the oven. The hydrothermal treatments were carried out from 60-150°C. After the growth, the autoclave was allowed to cool down naturally. The samples were taken out, washed in the deionized water several times and dried in air.

The surface morphology and the crystalline quality were characterized by using a scanning electron microscope SEM, X-ray diffraction XRD, respectively. The photoluminescence measurement was carried out on the ZnO nanorods synthesized.

III. Results and discussion

1. Characterization of ZnO nanorods:

a) Morphology of ZnO nanorods

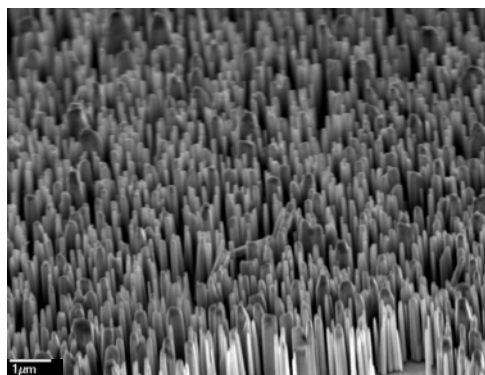


Fig 1: SEM image of ZnO nanorods with till angle

The ZnO nanorods were obtained at pH ~9-10, growth temperature 100 °C, with 0.25g zinc acetate concentration 0.016M. Figure 1 shows the SEM image of the ZnO nanorods, grown on the (0001) GaN substrate in 5 hours. The nanorods uniformly covered the entire surface with the hexagonal cross section and sharp tips. From the cross section image, the rods grew vertically from the GaN substrate, having uniform thickness and length distribution. The diameter and length of the nanorods are 80-120nm and ~1 μm, respectively. The hexagonal shape of the nanorods reveals that the rods grew epitaxially on the GaN film. The diameter, length and density of the ZnO nanorods can be changed by varying the growth time and reactant concentration. The nanorods with diameter 60 nm, length up to 2 μm can be achieved by increasing the reactant concentration to 0.021M and increasing the growth time to 7 hours.

b) Crystalline property of ZnO nanorods

The XRD measurement was carried out to characterize the crystal structure of the nanorods. During the measurement, the 2θ scan was used while the ω value was kept constant during the scan to avoid the GaN peaks from the substrate. From the XRD spectrum shown in figure 2, the strong peak at 2θ =34.42 due to ZnO (002) crystal plane was obtained from

which a lattice constant of 5.206 Å was estimated. In addition, small peak corresponding to the ZnO (004) crystal plane was also observed. The strong (002) diffraction peak is consistent with the SEM images which demonstrate the oriented arrays of ZnO nanorods with a preferential growth in the c-axis orientation. All the observed diffraction peaks can be indexed to the hexagonal phase of ZnO.

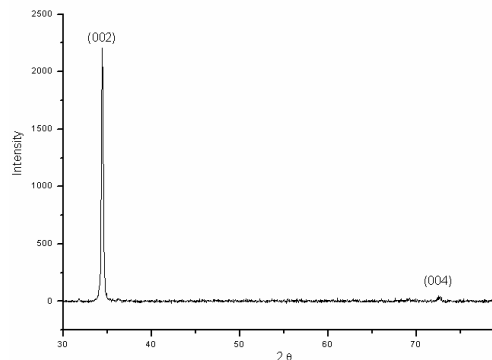


Fig 2: XRD spectrum of ZnO nanorods on GaN

c) Optical properties of ZnO nanorods

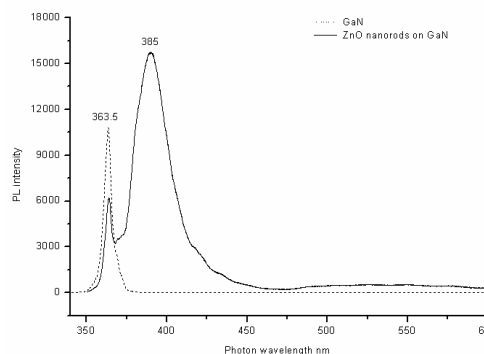


Figure 3: The photoluminescence spectra of ZnO nanorods (full line) and GaN substrate (dot line) at room temperature

As a potential photonic material, it is important to evaluate the optical properties of ZnO. Photoluminescence measurement was performed on the ZnO nanorod/GaN substrate since it is an effective method to investigate the presence of defects. Figure 3 shows the PL spectrum of the ZnO nanorods grown on GaN substrate (full line) and the PL spectrum of GaN substrate (dot line) at room temperature. The PL spectrum of the GaN substrate was obtained by removing the ZnO nanorods from the small area of the ZnO nanorods. The nanorods exhibit a sharp peak in the vicinity of the band edge at 385 nm (3.23eV). This peak is attributed to the exciton related recombination¹⁴. In addition, the small peak at 363.5 nm was also observed. This peak comes from the GaN substrate due to the fact that the ZnO nanorods did not cover the entire GaN surface. Besides, the defect peak was also observed, centered at 520nm (2.38eV). This peak is attributed to singly ionized oxygen vacancies in ZnO and the emission

results from the radiative recombination of a photogenerated hole with an electron occupying the oxygen vacancy¹⁵⁻¹⁶. To our knowledge, our ZnO nanorods have the highest intensity ratio of the band edge emission to the deep level emission among those obtained by solution methods.¹⁷⁻¹⁸

d) Growth mechanism of ZnO nanorods

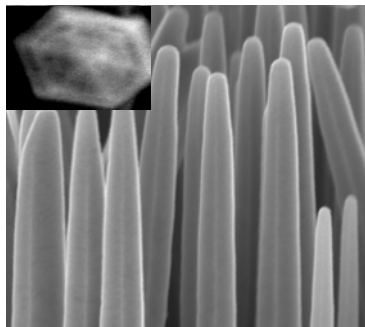


Figure 4: SEM image of ZnO nanorods with till angle at high resolution. The inset shows the shape of the nanorod's tip.

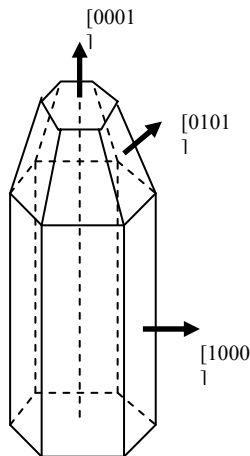
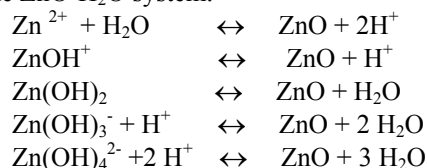


Figure 5: A schematic sketch of an ideal hexagonal rod

Next, the growth mechanism of ZnO nanorods in aqueous solution is discussed. The principle of aqueous solution techniques is based on heterogeneous nucleation and subsequent crystal growth on a specific surface. The heterogeneous nucleation is induced in supersaturated solution at a relatively low degree of supersaturation. The condition of the aqueous solution can be controlled by adjusting the reactant concentration, growth temperature, and the pH. Meanwhile, the crystal phase of the deposits was mainly determined by the pH of the aqueous solutions. If the pH is in the range 6 to 9, the Zn(OH)₂ is predominantly formed. The wurtzite ZnO crystal is formed at pH 9-13¹⁹. In the progress of the formation of ZnO, the complex Zn(NH₃)₄²⁺ or Zn(OH)₄²⁻ was formed first. Below is the thermal equilibrium of the ZnO-H₂O system:



With increase in temperature, these complexes will be dehydrated. And then, the ZnO crystal formed heterogeneous nucleus at the interface between substrate and solution. After that, the crystals begin to grow into the nanorods.

From Figure 4, the ZnO nanorods grown on the GaN have the hexagonal cross section and the well faceted prismatic morphology at the tip. The possible mechanism suggested is that the formation of hexagonal shaped of ZnO rod-like crystal is attributed to the difference in the growth

rate of the various crystal facets, resulting the crystallite shape observed²⁰. The relative growth rate of these crystals faces, which can be adjusted by the growth conditions, will determine the aspect ratio of the ZnO nanorods. Fig 5 shows the schematic sketch of an ideal ZnO rod. Growth in the <001> direction has the fastest growth rate. Growth in the <101> direction has intermediate growth rate, and in the <100>, the growth rate is smallest. Hence, the relationship of the growth rate of ZnO crystal face is $R_{\langle 001 \rangle} > R_{\langle 101 \rangle} > R_{\langle 100 \rangle}$. These relationships will result in the formation of 1-D ZnO nanorods with hexagonal cross section.

2. Effect of ZnO nanorod morphology on growth temperature: from nanoneedles to nanorods

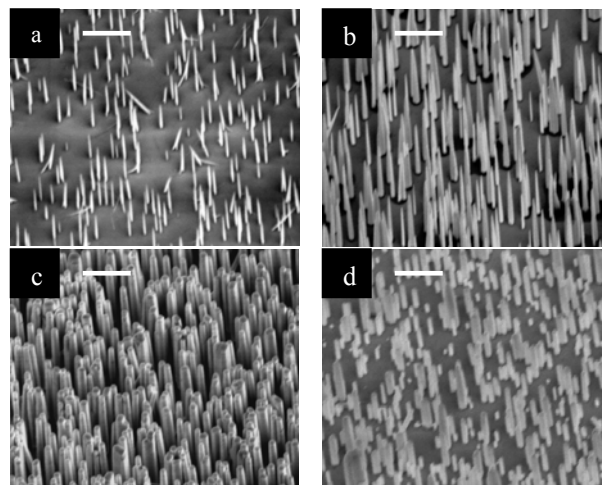


Fig 6: ZnO nanorods grown on GaN with different growth temperature : (a) 60°C , nanorod density $3 \times 10^4 \text{cm}^{-1}$ (b) 80°C , nanorod density $7 \times 10^4 \text{cm}^{-1}$ (c) 100°C , nanorod density $2 \times 10^5 \text{cm}^{-1}$ (d) 150°C , nanorod density $1.2 \times 10^5 \text{cm}^{-1}$. (scale bars are 1 μm)

In the case of ZnO growth using aqueous solution, the 1D growth can be enhanced at the certain growth parameters (pH, reactant concentration, growth temperature). The dependence of ZnO nanorod morphology on the growth parameters has been investigated. The growth temperature, reactant concentration (zinc acetate concentration), pH were changed so that the optimum value of growth parameters can be obtained. However, in this paper, only the temperature dependence was presented due to some interesting results.

The growth temperature was changed from 60°C to 150°C while other parameters (reaction concentration Zn(CH₃COO)₂ · 2H₂O 0.25g , pH NH₄OH 0.85ml , growth time 5hours) were kept constant. The ZnO nanorod result was shown on Fig 6. From figure 6, the morphology of the ZnO nanorods change from sharp tip with high aspect ratio to flat tip with smaller aspect ratio when the temperature was varied from 60°C to 150°C. In addition, the density of the nanorods was also affected. The temperature at 100°C seems to be the optimum value in order to obtain high density of nanorods

(2.10^5cm^{-1}). The possible reason for these observed morphologies is the dependence of the relative growth rate of the crystal faces on growth temperature.

Figure 7 shows the cross section image of the ZnO nanorods at growth temperature 100°C and 80°C . The average

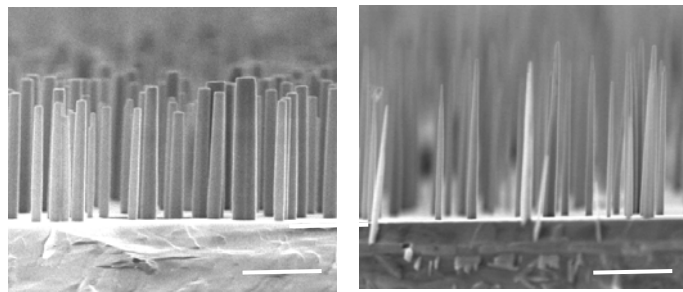


Fig 7 : the cross section SEM images of ZnO nanorods with different morphology : (a) ZnO nanorods with flat tip , growth temperature 100°C (b) ZnO nanorods with sharp tip , growth temperature 80°C (scale bars are $1\mu\text{m}$)

diameter and length of the nanorods are 90nm and $1.5\mu\text{m}$, respectively. The diameter of the nanorods grown at 80°C is a bit smaller, around $70\text{-}80\text{nm}$. These two kinds of morphology are found to be useful in laser and field emission application.

From figure 7a, all the nanorods have flat tips which can serve as miniaturized fabry perot optical cavities. Due to the fact that the incident light into the ZnO nanorods can not escape from the medium because of large difference of reflective index between air ($n_r = 1$) and ZnO ($n_r = 2.45$), the UV lasing emission can be generated.

The morphology of the ZnO nanorod (with sharp tip) in Fig 7b is useful for field emission application. Beside the sharp tip and high aspect ratio, ZnO is well known having negative electron affinity, high mechanical strength and chemical stability. With these properties, ZnO has a potential in vacuum microelectronic devices (field emission display, x-ray sources...)

IV. Conclusion

A mild template-free aqueous route was successfully established to synthesize vertically aligned ZnO nanorod arrays. From the SEM, XRD measurement, the ZnO nanorods are seen to be vertically well-aligned in the c-axis orientation, have uniform hexagonal structure with diameter of $80\text{-}100\text{nm}$ and length of about $1\mu\text{m}$. The photoluminescence measurement also exhibit strong exciton related emission with weak defect peak, which showed that the nanorods have good optical properties with low atomic defect. In addition, the growth mechanism of the ZnO nanorods had also been discussed.

The change of ZnO nanorod morphology from nanoneedle to nanorod was also observed when the growth temperature was changed from 60°C to 150°C . This offer a flexible method to obtain ZnO nanostructure with different shapes (needle, rod) for different application (field emission , laser application)

With further improvement, the vertically aligned ZnO nanorods epitaxially grown on the GaN substrate seem to be the promising method to fabricate of the p-n heterojunction nanorod devices. Further works are also needed to explore the lasing emission and field emission properties of the ZnO nanorods.

V. References:

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