Synthesis and photoluminescence properties of ZnO nanohelices

M Y Zhou¹³, L S Qu¹ and H Gao²
¹Naval Aeronautical and Astronautical University Department of Basic Sciences, Yantai, Shandong 26400, P.R. China
²Department of Physics, Harbin Normal University, Harbin, Heilongjiang 150080, P.R. China
E-mail: zhoumingyu_2004@163.com

Abstract. Sb-doped zinc oxide nanohelices were synthesized on silicon substrates by chemical vapor deposition. The morphologies and structures of the samples have been investigated by XRD, SEM, and HR-TEM. The ZnO nanohelices have a single crystalline wurtzite structure. Its length is up to tens of micrometres as a whole. It grows in the direction of (0001). There are six sticks in each period of the helices, which grow along six directions of the equivalent \( \langle 0 \overline{1} \overline{1} \rangle \). In addition, its growth mechanism is discussed. Optical properties of the nanohelices were demonstrated by Photo-luminescence (PL) spectra.

1. Introduction
ZnO with a high band gap (3.37eV) and exciton binding energy (60 meV) has been researched widely because of its broad range of applications. In particular, the application of low voltage and short wave optoelectronic devices has attracted more and more attention. ZnO has the structure of wurtzite, which is simply depicted schematically as lots of alternating planes consisted of tetrahedrally coordinated \( \text{O}^{2-} \) and \( \text{Zn}^{2+} \) ions, Selective stacking growth along the c-axis [1]. Because of their originality properties and application possible in electronics, optoelectronics, electromechanics[2], one-dimensional ZnO nanostructures has created wide comment. For one-dimensional nanostructures, their morphology determines their possible applications.

Different morphologies were synthesized successfully, such as nanorings [3], nanocastles [4] and nanocombs [5]. Among these morphologies, ZnO nanohelices have been reported also. It is likely that different growth mechanisms are dominant for different materials but the addition of some foreign materials into the sources can help to form nanohelices[6-8]. In our experiment, Zinc Oxide source was added to Sb and the nanohelical structures were produced. The nanohelice is a part of a family of ZnO ribbon-like nanobelts. But unlike the elastic nanosprings it has been reported, the nanohelice is rigid. These uniform nanohelices may have the potential utilization of nano-size gas sensor, piezoelectricity and wave absorption. Its spread foreground in application was prospected.

2. Experimental
Put the ZnO and Sb precursors in alumina plane, which was located at the center of a horizontal tube furnace. The furnace chamber was heated up to 13000C, and had been mingled with molar ratio 70:1 before, The alumina tube was first evacuated to vapor pressure of 6.0 Pa to remove the residual...
oxygen under an N2 carrier gas of 75 sccm. In order to collect gray–black ZnO precursors, Covered with a 3nm thick Au layer the Silicon substrates were placed in the downstream area of carrier gas. The pressure was maintained at 3000 Pa and N2 was blown at a speed of about 100 sccm for ten minutes. When the furnace temperature dropped to room temperature, it can be find the white growth on the Au coated Si substrates. The as-prepared products were characterized and analyzed by X-ray diffraction(XRD), the scanning electron microscopy(SEM), Transmission electron microscopy(TEM) and high-resolution transmission electron microscopy(HRTEM). The Photoluminescence measurement was accomplished under the condition of room temperature by He-Cd laser.

3. Results and discussions

XRD spectra of ZnO nanohelices (Figure 1). The main diffraction peaks corresponds to the faces of ZnO crystal. In the samples, the diffraction peaks were not found from Zn or Sb.

![Figure 1. XRD pattern of the as-formated ZnO nanostructures.](image)

![Figure 2. (a) SEM image of a ZnO nanohelice; (b) A uniform ZnO nanohelix with right hand roller.](image)
Figure 2(a) shows the general morphology of the as-formatted sample from the low magnification SEM image. 1D ZnO nanowires were synthetized, yield up to 8%. The nanostructures are helices with lengths of several tens of micrometers. It shows distinctly that the nanohelices are concordant by High magnification SEM image from Figure 2(b). The pitch distance L, mean diameter D and the width of the nanowires of one ZnO nanohelice are uniform. They are range between 400-1000 nm, 200-300nm, 100-300nm, respectively. The nanohelices are almost hexagonal in cross-sections indicating that the axis of the nanohelix maybe grows along <0001> directions of Zinc Oxide. A period of six equal length pieces forming a helix. It may be pointed out that nanohelices can convert from right to left, or contrary. These helical structures gradually become loose, and even becomes curved nanowires.

Detailed structural of the nanohelices was further carried out using TEM. The transmission electron microscope images (Figure 3(a)) show that the angle between the direction of growth and the direction of axial is about 47°.

![Image](a)

![Image](b)

Figure 3. (a). The structure of ZnO nanohelix under transmission electron microscope(TEM); (b). HRTEM images indicated at the connection between two borders on pieces near the outer surface.

An HRTEM image (Figure 3(b)) indicated at the connection between two border on pieces of the nanohelices shows the apparently separated interplanar spacing of 0.26nm, corresponding to the (0002) lattice spacing which establishes that the helical structure has a dislocation free single crystal structure and that the nanohelices as a whole have an axis of <0001>. Based on images of SEM and TEM the theoretical angle between the <0111> and [0001] directions is 47.25°, it can be induced that the six pieces form the nanohelix structure grows in a spiral cycle along the six equivalent directions. Thus, the spiral surfaces of side should be composed of Zn²⁺ terminated \{0\bar{T}11\}, O²⁻ terminated \{10\bar{T}0\}, and nonpolar \{0\bar{1}1\bar{2}\} are in back or front. Every building block of the nanohelices is terminated by Zn-terminated surface. It has confirmed that the surfaces are chemical activity at the (0001) Zn-terminated, but the surfaces of \{(0001)\} O-terminated and nonpolar surfaces are inert \[9\]. Therefore, (0001) the surface will be lead growth along the direction of uniform spiral. To investigate the growth conditions for ZnO nanohelices, we changed the growth time, pressure, gas flux and the growth temperature and produced a series of samples. The results show that the induction of Sb added the raw powder is very necessary for formation of ZnO nanomaterials. Without Sb, only nanowires with a growth direction of [0001] can be produced \[10\]. Introduction of Sb obviously decreases the evaporation temperature of ZnO and provides a special growth kinetics overcoming the surface energy
barrier to form ZnO rectangular nanostick[11]. From the calculated results of the relevant change of electrostatic energy, the nanospiral is positive and favorable. It is worth noting that the ZnO nanohelices grow along the C-axis, and the length of obtained products could beyond several micrometers.

**Figure 4.** SEM images about SiO$_2$ nanowires in higher temperature zone.

The temperature of deposition is another important parameter influenced the morphology. What we discovered is that the ZnO nanohelices could only be fabricated at higher temp region about 1200°C. At high temperature deposition region, thermal disturbing caused the formation of ZnO nanowires or SiO$_2$ nanowires (in Figure 4). According to the preceding information, a Vapor-Solid growth mechanism of Sb induced synthesis is put forward. The mechanism for the growth of nanohelix in detail is still under study.

**Figure 5.** Room temperature PL curves of the as-synthesized ZnO helices.

Figure 5 shows the room temperature PL curves of the as-synthesized ZnO helices. What we analyzed is that the peak of near-band-edge ultraviolet (UV) at 384 nm is pretty strong compared with the green emission at 520nm, which is quite weak. It is usually believed that the oxygen deficiency in ZnO leads to the visible emission peak and the emission results from the radiative recombination of a photogenerated hole with an electron occupying the oxygen vacancy. The luminescence of the free exciton recombination causes the Ultraviolet emission [12]. For the PL spectrum of the nanohelices,
an intense single ultraviolet emission peak is situated at 384 nm, which can be attributed to the free excitonic recombination emission, while the deep-level emission corresponding to oxygen vacancies or surface state emission is barely observed, being much weaker than previously reported [13]. This fact of experiment shows the products’ good crystalline nature.

4. Summary and conclusion
To summarize, through the way of thermal evaporation to get the uniform ZnO nanohelices was fabricated. The nanohelices have a uniform period, a faultless hexagonal cross-sectional area and an \(\{0001\}\) axial growth direction. It is necessary for the induced Sb in the source material to form the helical structure, which is energetically favorable. In the different deposition temperature zone, different morphologies of ZnO nanostructures show that another factor in growth mechanism is deposition temperature. Due to the perfect periodicity of helical structure along the axis, it is hoped that it can be used in a photonic band-gap material. In the helical structure, it is possible to find some interesting phenomenon related to Faraday rotation effect, which might be possible used for building pieces in photoelectric devices and optoelectronic coupling system also.

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