Potential Applications and Synthesis of Zinc Oxide Tubes

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Abstract

Zinc oxide is a unique material that exhibits optical, semiconducing, piezoelectric, and magnetic properties. In the past decade, zinc oxide (ZnO) tubes are a newly-developing morphology with the special properties of low densities, thermal insulation, and high surface permeability. In light of wide potential applications of zinc oxide tubes, the applications and potential applications were reviewed in this paper. We have proposed a new and facile method to synthesize ZnO tubes in a large scale, which introduce ammonia water into zinc chloride aqueous solution. The advantages of our utilizing-aqueous solution-based method are template-free, surfactant-free, low temperature and normal pressure. The growth mechanism of ZnO microtubes have been proposed based on the experimental results and ZnO special polar property.

1. Introduction

Zinc oxide (ZnO) is a distinguished material with some special properties, which has attracted intensive research efforts for its unique properties and versatile applications in transparent electronics, ultraviolet (UV) light emitters, piezoelectric devices, chemical sensors and spin electronics in the last few decades. [1-12] ZnO is a wide band-gap (3.37 eV) compound semiconductor that is suitable for short wavelength optoelectronic application. The high exciton binding energy (60 mV) in ZnO crystal can ensure efficient excitonic emission at room temperature and room temperature ultraviolet (UV) luminescence has been reported in disordered particles. The lack of a center of symmetry in wurtzite, combined with large electromechanical coupling, results in strong piezoelectric and pyroelectric properties and the consequent use of ZnO in mechanical actuators and piezoelectric sensors. Based on these remarkable physical properties and the motivation of device miniaturization, large effort has been focused on the synthesis, characterization and device application of ZnO nano- and micro-materials.

This review paper describes traditional and novel synthesis techniques of tubular ZnO particles on the recently published works. The potential applications of ZnO particles in the various fields are presented.

2. Properties and potential applications of ZnO particles

a) Luminescent property

ZnO exhibits a direct band-gap of 3.37 eV at room temperature with a large exciton of 60 mV. The strong exciton binding energy, which is much larger than that of GaN (25 mV), and the thermal energy at room temperature (26 mV) can ensure an efficient exciton emission at room temperature under low excitation energy. As a consequence, ZnO is recognized as a promising photonic material in the blue-UV region.

b) Gas and chemical sensors

Conductometric metal oxide semiconductor thin films are the most promising among solid state chemical sensors, due to their small dimension, low cost, low power consumption, on-line operation and high compatibility with microelectronic processing. The fundamental sensing mechanism of metal oxide based gas sensors relies on a change in electrical conductivity due to the process of interaction between the surface complexes, such as O^-, O_2^-, H^+ and OH- reactive chemical species and the gas molecules to be detected. Oxygen vacancies on metal-oxide surface are electrically and chemically active. These vacancies function as *n*-type donors, often significantly increase the conductivity of oxide. Upon adsorption of charge accepting molecules at the vacancy sites, such as NO_2 and O_2, electrons are effectively depleted from the conduction band, leading to a reduced conductivity of the n-type oxide. On the other hand, molecules, such as

CO and H_2, would react with surface adsorbed oxygen and consequently remove it, leading to an increase of conductivity. As one of the major materials for solid state gas sensor, bulk and thin films of ZnO have been proposed for CO, NH_3, alcohol and H_2. [13-16]

c) Piezoelectric effect and polar surfaces

As one of the important properties of ZnO, its piezoelectricity has been extensively studied for various applications in force sensing, acoustic wave resonator, acousto-optic modulator, *etc.* [17-19] Piezoelectricity is due to atomic scale polarization. To illustrate the piezoelectricity, one considers an atom with positive charge that is surrounded tetrahedrally by anions, as shown in Fig.1. [20] The center of gravity of the negative charges is at the centre of the tetrahedron. On exerting a pressure on the crystal along the cornering direction of the tetrahedron, the tetrahedron will experience a distortion and the center of gravity of the negative charges will no longer coincide with the position of the positive central atom; an electric dipole is generated. If all of the tetrahedral in the crystal have the same orientation or some other mutual orientation that does not allow for a cancellation among the dipoles, the crystal will have a macroscopic dipole. The two opposite faces of the crystal have opposite electric charges.

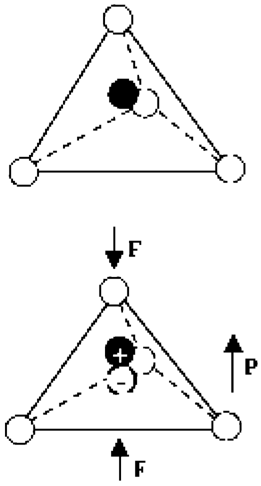

Figure 1 Schematic diagrams showing the piezoelectric effect in a tetrahedrally coordinated cation-anion unit

Another interesting result of the non-centrosymmetric ZnO crystal structure is its spontaneous polarization and polar face dominated nanostructure. [21, 22] The crystal structure of ZnO can be visualized in a way that oxygen atoms and zinc atoms are tetrahedrally bonded. These tetrahedrons stack along [0001] direction. Due to spontaneous polarization, the position of positive charge is displaced from that of negative charge and the direction of displacement is also [0001]. The net result of this spontaneous polarization is a charged (0001) surface.

3. Synthesis methods of tubular ZnO particles

Besides nanowires, nanobelts and nanorods, other complex ZnO nanostructures, such as tubular ZnO particles [23, 24] also attract considerable research interests. Since the discovery of carbon nanotube [25], several methods for fabrication of ZnO particles with tubular structure have been reported, such as vapor phase depositions, thermal oxidation, a template-assisted method and a hydrothermal process. A few of them are described in the followings:

A) The most common method synthesize ZnO nanostructure utilizes a vapor transport process. [26, 27] In such a process, zinc or zinc oxide and oxygen or oxygen mixture vapor are transported and react with each other, forming ZnO nanostructure. According to the difference on the formation mechanisms, the extensively used vapor transport process can be categorized into the catalyst free vapor-solid (VS) process [28, 29] and catalyst assisted vapor-liquid-solid (VLS) process [30]. The typical process is usually carried out in a horizontal tube furnace, as shown in Fig.2 [20], which is composed of a horizontal tube furnace, an alumina tube, a rotary pump system and a gas supply and control system. R.M. Wang has synthesized ZnO nanotubes through heating the mixture of Zn and ZnO powder at 1300˚C in Ar flow. [31]

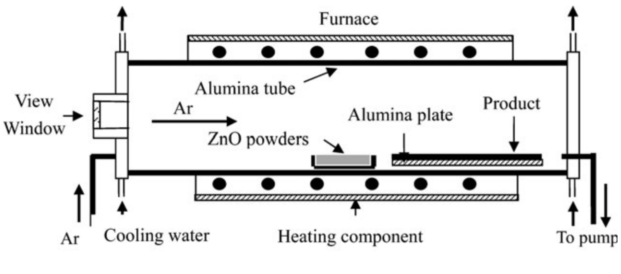

Figure 2 Schematic diagram of the experimental apparatus by the vapor transport process

B) Another evaporating synthesis method to synthesize ZnO particles is metal-organic chemical vapor deposition. [32] The typical diagrammatic sketch of metal-organic chemical vapor deposition (MOCVD) device system is shown in Fig.3. [33] In a typical CVD process, the substrate is exposed to the volatile precursor, which reacts or decomposes on the substrate surface to produce the high purity, high performance film. Frequently, volatile by-products are also produced, which are removed by gas flow through the reaction chamber. Through CVD method, the steams of volatile metal compounds or metal organic compounds is used as raw materials, and through chemical reaction made into the material needed. Then it condenses rapidly under protection of inert gases for preparation of particles. The ZnO particles prepared by CVD possess high purity, uniform particle size which can be accurately controlled. B. P. Zhang et al [34] have reported that ZnO tubes were epitaxially grown on sapphire (0001) substrate by MOCVD. The growth pressure and temperature were 0.3-3 Torr and 475°C, separately. Oxygen gas and diethyl zinc were used as precursors and nitrogen gas was used as the carrier gas for DEZn by-product.

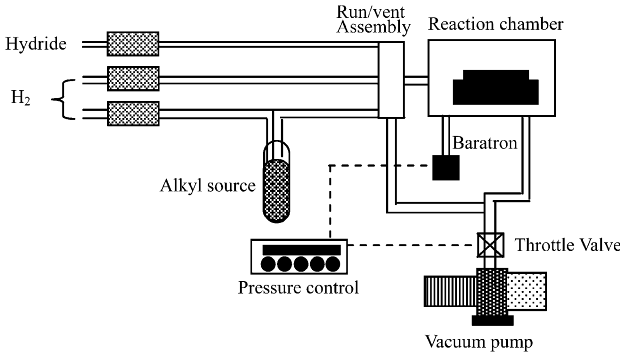

Figure 3 Diagrammatic sketch of atmospheric metal-organic chemical vapor deposition (MOCVD) device system

C) Other synthesis methods

Although the vapor transport process and hydrothermal method are the dominant synthesis processes for synthesis ZnO particles with tubular structure. Other growth methods such as hydrothermal methods [35, 36], replication and template techniques [37, 38] and laser patterning [39] have been developed in parallel. These methods provide the possibility of forming ZnO tubes at low temperature. For example, via a hydrothermal method [36], Vayssieres et al. have reported the synthesis of ZnO microtubes, on a range of substrates, immersed in a bottle with an autoclavable screw cap containing equimolar amounts of zinc nitrate and hexamethylenetetramine and maintained at 90°C for 2 days. Z. Wang and H. L. Li [38] have synthesized ZnO nanotubules via a sol-gel process within the pores of an anodic aluminum oxide (AAO) template.

4. The developed aqueous solution method

Rigid experimental conditions (such as high temperature), sophisticated equipments (such as autoclave), and complex procedure were usually employed in the above mentioned methods in order to obtain single-crystalline and high purity ZnO tubes. Furthermore, most of the reported approaches produced ZnO tubes in small quantities and high cost, restricting their commercial applications. So it is necessary to develop a template-free and surfactant-free method at low temperature, low cost and normal pressure.

In this paper, we proposed a new and facile method to synthesize the hexagonal ZnO microtubes in a large scale.[40-42] In comparison with other previous studies, we did not introduce any other chemicals except reactants in the reaction solution. Besides this, the advantages of our utilizing-aqueous solution-based method are template-free, surfactant-free, low temperature and normal pressure.

Figure 4 is the experimental procedure. The typical experimental procedures were as follows: the conical glass flask with the aqueous solution (400 ml) of zinc chloride (purity of 98 % from Wako, Japan), of which zinc ionic concentration is 0.5 M, was heated in the oil bath under stirring. Aqueous ammonia water (25 wt%) was added dropwise into the reaction solution with stirring, immediately resulting in the formation of white precipitates. When the pH of the reaction solution reached 7.5, the introduction of ammonia water was stopped. The precipitate was kept at reaction solution for different time, then filtered and dried.

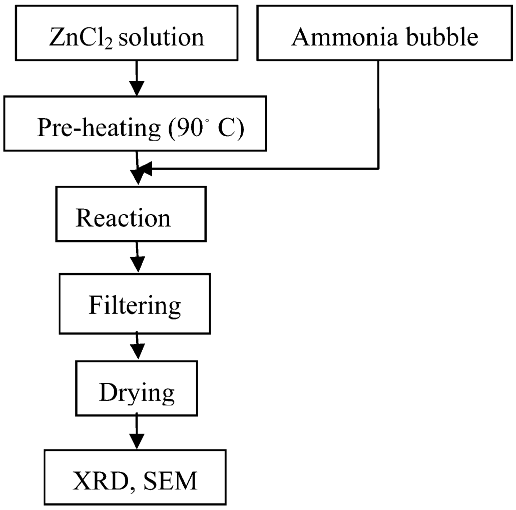

Figure 4 Experimental procedure

Figure 5 shows XRD patterns of wet samples with different aging time. The precipitates were filtrated and then analyzed using XRD. The products without aging are the hydrate of zinc oxide precursor. With the aging time increasing, the precursors turn into zinc oxide. Until the aging time is 8 h, the products still contain some precursor except zinc oxide.

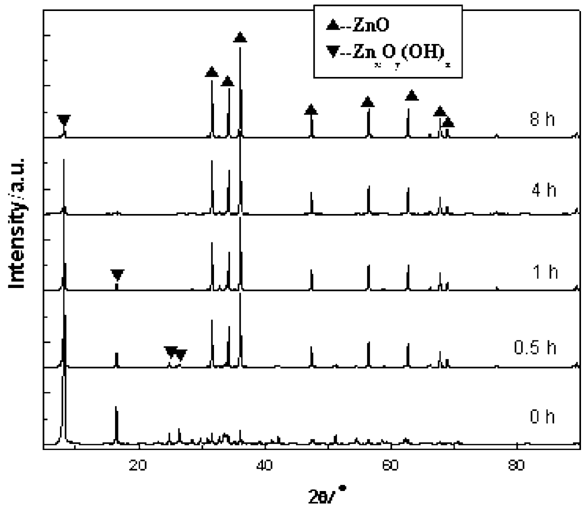

Figure 5 XRD patterns of wet samples with different aging time

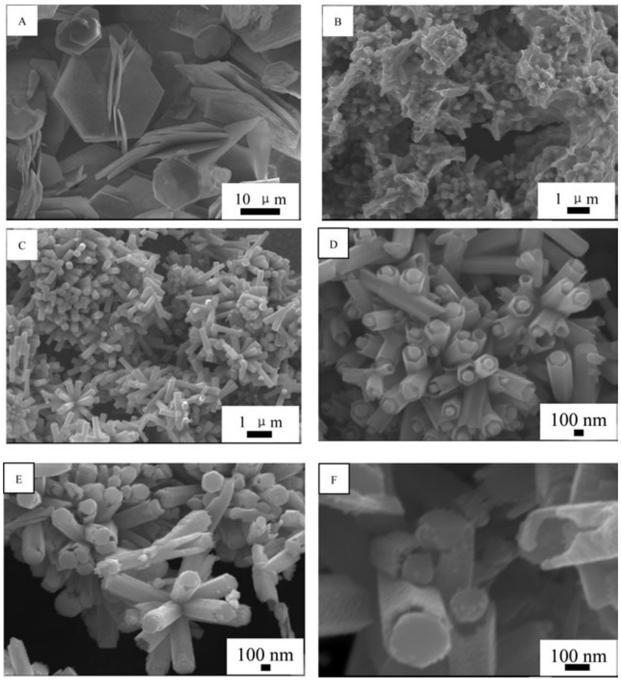

Figure 6 SEM and images of ZnO microtubes at different aging time

Figure 6 reveals the morphological evolution of ZnO particles from layer-like precursor to tube-like zinc oxide by adjusting the aging time. It can be clearly seen that layer-like particles with 10~12 μm in the length of layer-side were obtained without aging duration, shown in Fig.6 (A), which is the white precipitate directly filtrated after the reaction. While aging duration was 2 h, as shown in Fig.6 (B), layer-like particles began to decomposing into rod-like particles. In the decomposing layer structure, it is likely that some of rod-like just grow up. Fig.6 (C) shows SEM image of well hexagonal ZnO microrods formed when the aging duration for 6 h. Some of hexagonal rods assemble together and form flower-like structure. Fig.6 (D) show the morphologies of ZnO samples obtained after 3 days aging duration, the hexagonal shell peel with the column-like particles inside, which is the evidence of intermediate process in the second stage. The preferential chemical dissolution of the metastable (001)-Zn faces of the microrods shall lead to the tubular ZnO particles, as shown in Fig.6 (E) and Fig.6 (F). Figure 6 (F) shows the magnified images of ZnO tubes. The aging duration is that the systems will tend to reach their thermodynamic stability and may therefore undergo variations of morphology, size and structure properties.

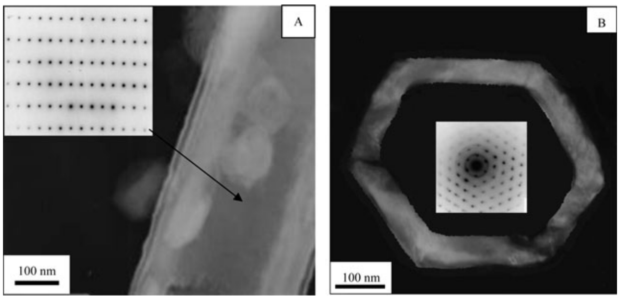

Figure 7 TEM images of ZnO microtubes

Figure 7 shows the further characterization of the prepared tubes using TEM. Figure 7 (A) is the TEM images of a horizontally cut tube. The dark center and bright edge indicates the presence of hollow structure inside of the tube. The small particles observed inside of the tube are believed to be the result of cutting. The inset of Fig.7 (A) is an electron diffraction (ED) pattern selected from the wall of tube, which reveals that the tube was single crystalline. The inset of Fig.7 (B) is an ED pattern selected from the hexagonal opening, which indicates that the tube is single crystalline and grew along [0001] direction (*c* axis).

In the progress of the formation of ZnO, the growth units $[Zn(NH_3)_4]^{2+}$ and $[Zn(OH)_4]^{2-}$ encapsulated by water were formed first. These growth units are easy to attach on the surface of precipitate. The formation of hexagonal ZnO microtubes is attributed to the different growth rate of the various crystal facets and the polar (0001) surface. Generally, the growth rate of ZnO crystal in the aqueous solution in the [0001] direction is about twice as fast as that in the $\langle 01\bar{1}0\rangle$ direction. [43] That is due to (0001) surface has roughly a 60 % higher cleavage energy than the nonpolar $\{01\bar{1}0\}$ facets [44], which results in the higher growth rate along the [0001] direction with the formation of unstable surface. According to classical crystal growth theory, a crystal facet grows rapidly, and easily disappears from the final crystal morphology. Finally ZnO microtubes were formed by the dissolution of unstable (0001) surface. Figure 8 shows schematic illustration of possible growth mechanism for ZnO microtubes.

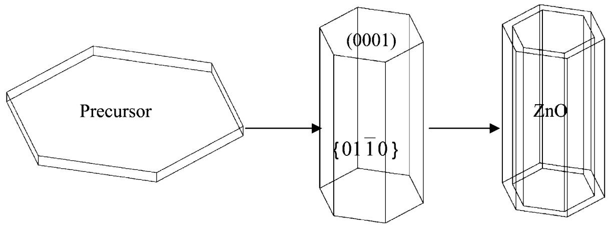

Figure 8 Growth mechanism of ZnO micro-tubes

4. Summary

This paper reviews the potential application of zinc oxide particles in the semiconducting, piezoelectric and optical fields and discusses until now the traditional techniques for the synthesis of zinc oxide tube. These methods involve rigid conditions, sophisticated equipments and complex procedure. Our developed aqueous solution method is a facile and new process to synthesize ZnO tubes with the characteristic of low cost and high production.

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