SYNTHESIS OF ZnO NANOWIRES USING BALL-MILLING AND ANNEALING METHOD

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ABSTRACT

Nanowires represent a new class of ZnO morphologies with many exiting new properties and applications. The research in the synthesis and characterization of ZnO nanowires has received enormous attention in recent years. However, most synthesis methods using vapor deposition process can only produce small amount of sample, mass production has not been achieved yet. Large-quantity production of ZnO nanowires needs to be realized for large-scale property and application studies. One of the promising approaches to the large scale synthesis is a ball-milling and annealing method. This paper first introduces several common synthesis methods of ZnO nanowires and then summarizes the one dimensional nanomaterials produced by the ball milling and annealing method. Finally, some preliminary results of ZnO nanowire synthesis are presented.

1. INTRODUCTION

Zinc oxide (ZnO) is an important semiconductor with a wide band gap of 3.37 eV at room temperature. Owing to the asymmetric wurtzite structure, ZnO is a unique material for optoelectronics, lasing and piezoelectricity. The structure of ZnO can be described as a number of alternating planes composed of tetrahedrally coordinated O²⁻ and Zn²⁺ ions, stacked alternately along the c-axis. The oppositely charged ions produce positively charged Zn-(001) and negatively charged O-(001) polar surfaces, resulting in a normal dipole moment and spontaneous polarization along c-axis. One dimensional (1D) ZnO nanowires grow in most cases along [001] direction (parallel to the c-axis) and thus have a hexagonal cross section. Some ZnO nanowires have a rectangular cross section and one of three typical growth directions, and are called nanobelts.

ZnO nanowires and nanobelts are considered to be used as active component elements and interconnections in nanoelectronics. Prototypes of nanowire based transistors and light-emitting diodes have been demonstrated, and simple nanowire based circuitry has also been created. In addition, ZnO nanowires are shown to be efficient nanoscale lasers and can be used as light sources, waveguides and optical switches in nanoscale optics. Other applications include catalysts, sensors, piezoelectric transducers, transparent conductors, surface acoustic wave devices, and the electrodes of solar cells.

Although several methods have been developed in the synthesis of ZnO nanowires, large scale fabrication still remains a challenge. Large amounts of the nanowire material are crucial for testing properties and possible applications at large scale. Therefore, a mass production method of ZnO nanowires must be developed. One of the promising methods for large scale nanowire production is a ball-milling and annealing method which is described in this paper.

This paper first describes the current common synthesis methods of ZnO nanowires, and then summarizes the fabrication of various nanowires produced using the ball milling and annealing method. Finally, preliminary results of the synthesis of ZnO nanowires using ball-milling and annealing method conducted by us are described.

2. SYNTHESIS METHODS OF ZnO NANOWIRES

1D ZnO nanostructures have been extremely popular materials in the last five years and more than 500 papers have been published on this topic. Most of them deal with the nanowire synthesis. Different research groups use different synthetic methods. Most popular methods are vapor phase deposition, metalorganic chemical vapor deposition (MOCVD), hydrothermal solution approach and template-assisted sol-gel process and electrochemical deposition.

The vapor phase deposition is the most common method. In this approach, precursor material vaporizes in the high-temperature zone of a tube furnace and the vapor is transported by a carrier gas or by diffusion to the substrate placed at a lower temperature zone. The growth of ZnO nanowires produced in the vapor deposition method is interpreted by either vapor-solid (VS) or vapor-liquid-solid (VLS) mechanisms. In the case of the VS growth, ZnO nanowires form directly from the gas vapor phase by the condensation of the vapor. Pure ZnO nanowires can be obtained as metal catalysts are not used. However, the morphology of the final crystals is very sensitive to the growth conditions and some catalysts have to be used to help the formation of one-dimensional morphology. In such case, a different growth mechanism, VLS process,
controls the growth process. In a typical VLS process, the gaseous reactants from the vapor dissolve into nanosized liquid droplets of a catalyst, followed by nucleation and growth of single crystalline wires through precipitation from the oversaturated solution. Au, Cu, Ni and Sn are widely used typical metal catalysts for ZnO nanowire growth. Recently, Z.W. Pan et al. reports that the growth of ZnO nanowires can be also governed by Ge particles, which is the first semiconductor catalyst reported. A catalyst can be evaporated together with the source materials or pre-patterned on the substrate surface. The equipment required by this method is an atmosphere-controlled tube furnace. The production process is relatively simple and the cost is low. It is possible to scale up for producing more samples.

Metalorganic chemical vapor deposition (MOCVD) is an alternative approach to produce nanowires and nanorods. In this approach, metalorganic precursor decomposes/reacts with oxygen to yield the desired nanorods/nanowire composition. Two types of precursors are typically used – diethylzinc (Zn(C₂H₅)₂) and O₂/N₂O or zinc acetylaconate hydrate and O₂/N₂ mixture. The advantages of this method are precise control of nanowire length, relatively low formation temperature (400-700°C), high efficiency of oriented growth and compatibility with existing technology used in electronics. Most products of MOCVD are relatively short oriented nanorods with sharp or flat tips and can be deposited on various substrates of Si, Al₂O₃, GaAs or fused silica. Production of long nanowires had been a challenge to the MOCVD method. Recent modification of the growth conditions has produced long nanowires with or without the use of catalysts. Because of the sophisticated equipment of the MOCVD reactor, the quantity of the nanowires is low and the cost is high compared with the vapor-deposition process.

Another common approach to synthesize ZnO nanowires is the solution process, in which the Zn(NH)₄²⁺ and Zn(OH)₂⁻ complexes, as precursors, decompose in various solutions. Hydrothermal conditions are used in most cases to generate the growth of ZnO nanowires. The advantage of a solution approach is a low growth temperature and perspectives for relatively larger quantity production. To enhance the formation of nanowires and to suppress the formation of other morphologies, some special strategies are applied in the solution method, including the use of preliminary deposited nanoparticles of ZnO as growth seeds, the application of microemulsions and various surfactants to promote 1D growth. When microemulsion is used, every microemulsion droplet acts as a nanoreactor for the formation of nanoparticles. When different droplets coalesce, nanoparticles can attach to each other by means of “oriented attachment” mechanism. Cetyltrimethylammonium bromide (CTAB), PVP and polyethylene glycol (PEG) are used as typical surfactants. They can interact with different surfaces of the crystal in a different way or form rod-like micelles that act as templates for wire growth. By suppressing the growth of some crystal planes, carbamide can provide the formation of ZnO nanobelts in a solution.

The fourth approach is the use of templates of cylindrical channels. Three kinds of such templates are typically used – anodic alumina membranes, polycarbonate membranes and mesoporous silica. The synthesis of nanowires in these templates is performed by sol-gel or electrochemical deposition methods. The first successful synthesis of ZnO nanowires by sol-gel synthesis inside of a template was performed in 1997, which is much earlier than other methods. However, electrodeposition and sol-gel processes usually produce only nanowires with a polycrystalline structure instead of single crystalline as produced by other methods. Another drawback is the necessity to get rid of the template after the synthetic procedure. Nevertheless, the production of single crystalline ZnO nanowires by electrodeposition without using a template with channels have been reported recently.

Large scale synthesis of ZnO remains a very important issue. A large scale testing of properties and any proposed applications are impossible without the capability to produce material at least in gram or kilogram quantities. However, the above methods can produce small amount of samples typically at milligrams order. Only minor progress has been achieved in this direction. Z.F. Ren et al. reported the possibility to produce gram quantities of ZnO by vapor deposition method. The key step is the use of porous graphite substrates (such as graphite flakes or carbon cloths) instead of flat substrate. Such porous substrate has a relatively large surface area and can greatly enhance the yield of nanowires. The residual carbon support can be burnt away easily. Therefore, real large scale production up to kg requires more research efforts and novel approaches.

An alternative way to produce large amounts of nanowires can be the ball-milling and annealing method. Large quantities of BN nanotubes and CₓNᵧ nanorods have been produced by this approach recently. It is possible that the method can be modified to yield large quantities of nanowires of other materials including zinc oxide. The next section of the paper reviews the synthesis of nanowires by the ball-milling and annealing approach.

3. BALL-MILLING AND ANNEALING METHOD

A two-step process consisting of ball milling and annealing was first developed in 1999 in synthesis of C and BN nanotubes, and it has been shown recently as an efficient way to enhance the growth of other one-dimensional nanostructures. The first step in this method is a mechanical treatment of a precursor powder or/and synthesis through a mechanochemical reaction. The obtained product can be annealed at an elevated temperature to yield the desired product. Such
a method can be potentially applied to the growth of large quantities of nanowires of various materials.

Mechanical treatment in ball mills is well known to be an efficient way for the synthesis of various metastable phases (including high temperature and high pressure ones) and induction of solid-solid, solid-liquid and solid-gas chemical reactions which do not normally happen at room temperature. Mechanical milling typically leads to a decrease of crystallite size, a greater increase of the surface area of powders, the changes in chemical reactivity and volatility of the materials, and highly homogeneous mixing of components. The appearance of contaminations in the form of small metal particles from the container and ball materials is not always a drawback and can be beneficial for some particular syntheses as well.

The effects provided by ball milling have been proved to be helpful for the synthesis of one-dimensional nanostructures. Nanowires and nanorods of ZnO, SnO2, Ga2O3, GaN, AlN, GaP, C3N4, SiC, HfB2, ZrB2 and CdSe and nanotubes of BN and SnO2 have been synthesized by annealing of pre-milled corresponding powders.28-38 Despite of the large variety of materials obtained, the important effect of ball milling has not been carefully investigated. Special properties of the milled materials induced by mechanical milling, which have been proved to be beneficial for nanowire/nanotube growth, are discussed below.

As a result of mechanical milling, powders have smaller particle sizes and much higher surface areas. This usually leads to improved volatility and chemical reactivity of powders obtained in comparison with original commercial powders. The effect of higher volatility induced by ball milling can be used to grow nanowires in the vapor deposition method at a lower temperature. As a consequence of modified volatility, nanowires can be successfully grown at a lower temperature or under the conditions at which the formation of nanowires is normally impossible. For example, nanowires of ZnO, SnO2, Ga2O3, GaN and GaP were successfully grown from the ball-milled powders.28-32 Ball milling treatment helps the formation of single crystalline nanowires. For example, only polycrystalline curled GaP nanowires or ZnO plate-shaped chips were obtained by vapor deposition of unmilled GaP and ZnO powders, while high-quality single-crystalline nanowires or nanobelts were grown from milled powders at the same synthesis conditions. Ga2O3 nanobelts32 and GaN nanoribbon rings33 were obtained from milled GaN samples evaporated at 930-940°C. In contrast, no 1D nanostructures were grown from unmilled samples due to insufficient vaporization ability of initial GaN powder. These results show that ball milling enhance the growth of 1D nanostructures.

The smaller size, higher surface area and new metastable structure of milled powders also lead to higher chemical reactivities. In some cases, high chemical reactivity is further increased by a large number of structural defects induced by ball-milling. SiC nanowires and nanowire networks were produced by Z.J. Li et al.35 from ball-milled powders in the graphite reaction cell. The mixture of milled Si and SiO2 powders was used as precursor material to generate SiO vapor which is essential step for the synthesis. Preliminary ball milling treatment appears to be a key stage because no nanowires grow out without the milling treatment. This effect was attributed to the modified chemical reactivity of the powders after ball-milling.

Various metastable phases can be produced via structural disordering and mechanochemistry inside ball mills. These phases possess excessive energy and tend to recrystallize at moderately temperatures to yield thermodynamically stable products. This crystallization behaviour can be controlled by the variation of annealing conditions and may lead, at least for some materials, to 1D morphology. Such solid-state transformation of a metastable milled precursor was found to occur for BN nanotubes24 and C3N4 nanorods25.

BN nanotubes were synthesized in large quantities (up to 1 kg) by Y. Chen et al.24. The initial precursor represents mechanically disordered nanoporous BN or N-containing B powder produced by the mechanical treatment of boron powder in ammonia atmosphere. Such amorphous powders are metastable and undergo solid-state crystallization upon annealing conditions. Some nanotubes can grow catalytically on metal particles which are milling contaminations. Such a synthesis can be based, therefore, on the combination of two effects provided by ball milling, metastability of preliminary products and homogeneous introduction of small metal particles which can act as catalysts.25 Using the same method, C nanotubes were also produced.27 Carbon nitride precursor for the synthesis of C3N4 nanorods is produced by a mechanochemical reaction between ammonia and mechanically disordered carbon powder.26 The material obtained is metastable and can recrystallize into nanorods during the annealing in NH3 atmosphere. The rod-like hexagonal morphology of C3N4 is explained by the “lowest energy” arguments. The growth rate of [001] direction is found to be more than twice faster than those for other directions and stacking along the [001] direction is considered to be energetically favourable.

The effects of mechanical treatment favoring the formation of nanowires are not clearly defined in some cases. However, if ball milling obviously helps the growth of nanowires, it might be attributed by combined effects of various phenomena induced by the mechanical treatment. For example, milling of HfCl4/B mixture was found to be beneficial for the formation of HfB2 nanorods36. Annealing of unmilled samples also leads to the formation of HfB2 rods but with a lower yield and a wider diameter distribution. The positive influence of ball milling in this work is attributed to a
combination of an excellent mixing of components, the increase of surface areas of powders, mechanochemical reactions and the presence of contaminating Fe nanoparticles.

Micro- and nanoneedles of CdSe and micro- and nanotubes of SnO$_2$ are produced by J. Pique ras with coauthors$^{37,38}$ by evaporation of compacted milled and unmilled powders on the surface of compacted disks. Micro- and nanostructures were grown both from unmilled and milled samples but the amount of 1D structure is higher and their morphology is more homogeneous in the case that mechanical milling is used. The positive influence of mechanical treatment can be attributed to a combination of a higher volatility and the increase in the number of defects and small crystals with orientations favorable for 1D structures growth.

As can be concluded from the above discussions, the combination of mechanical milling with subsequent annealing can be applied for the production of large quantities of 1D nanostructures. This was already achieved for BN nanotubes and C$_3$N$_4$ nanorods by the solid state transformation of milled powders into 1D structures. It is believed that large scale approaches including a ball-milling step can be extended and modified to produce nanowires of a variety of other systems. The next section reports some preliminary results of our group on the fabrication of ZnO nanowires using the ball-milling and annealing method.

4. SYNTHESIS OF ZnO NANOWIRES BY BALL MILLING AND ANNEALING METHOD

We believe that two possible effects of ball milling can help to produce ZnO nanowires during the subsequent annealing. First, a milled powder often represents an amorphous or highly disordered nanocrystalline phase which is thermodynamically metastable, and must undergo a recrystallization to a thermodynamically favorable state upon annealing. If some nanoparticles or catalysts are introduced into the starting material, they may act as seeds that promote the formation of one-dimensional structures (nanowires) during annealing. Secondly, a milled powder has a different vaporization temperature and a higher volatility. This allows us to produce nanowires more efficiently at a lower temperature using the vapor deposition method.

To test these ideas, we prepared a precursor by ball milling. Zn powder with 6 at\% of Ge was milled for 100 hours in oxygen atmosphere with a steel rotating ball mill. Fig. 1a represents X-ray diffraction (XRD) pattern of as milled sample. Only broad peaks of ZnO and a very small peak of Zn can be observed, suggesting nearly complete oxidation of Zn powder induced by ball milling. No Ge peaks are found in the pattern, which can be explained by a low Ge content in the sample or overlapping with the broad ZnO peaks. However, Ge is obviously present in the sample since it can be detected by X-ray energy dispersive spectroscopy (EDS). The broadened diffraction peaks of ZnO indicate small crystallite size and possible high level of structural defects, as the consequence of room-temperature oxidation induced by ball milling. The as-milled samples were loaded in a ceramic combustion boat and placed in the middle of a tube furnace for subsequent annealing.

The milled powder was annealed first at low temperatures of 800 and 1000$^\circ$C in argon atmosphere. However, no nanowires were found after heating. Scanning electron microscopy (SEM) images in Fig. 2 show particle morphology of the heated two samples. Comparing the XRD patterns between the milled sample (Fig. 1a) and the sample heated at 1000$^\circ$C (Fig. 1b), the sharper and pronounced ZnO peaks in Fig. 1b suggest that crystallization occurred during the heating and large crystallites are formed in three dimensions instead of one-dimension as expected. Low annealing temperature might be responsible.

The same milled sample was heated at a higher temperature of 1300$^\circ$C in Ar flow. At this temperature, some ZnO should be vaporized and deposits were found on the Si wafer surfaces, which were located downstream 10-19 cm away from the sample. Although only particles were found in the combustion...
boat, nanostructures including thin nanowires are formed on the Si substrate. The morphology of the final product depends on the temperature zone of the substrate. Long nanowires were formed on the substrate located in the temperature zone of 250-350°C. Typical nanowires are shown in Fig. 3.

Figure 3. SEM image of nanowires obtained from ZnO-Ge milled system

Long (up to several micrometers) nanowires of diameter of 10-40 nm are found in large density on the wafer. The uniform diameter of the nanowires does not suggest any catalytic role of Ge particles as large Ge particles should be attached at the tip of the nanowires. Further analysis is required to find Ge particles in the sample. Almost no difference is found between the XRD patterns (Fig. 1b and 1c) taken from the annealed samples (residual samples in the combustion boat) heated at 1000 and 1300°C. Again, the grain growth took place during the heating along with vaporization. However, catalysts (Ge) failed to act in promoting 1D crystal growth. Different catalysts will be used to produce mass quantity of ZnO nanowires. The vapor-deposition process occurred at 1300°C produces thin ZnO nanowires. Compared with commercial ZnO powder without any milling treatment, the milled ZnO powders produce the nanowires with uniform size and well-crystallized structures in a higher density after heating at 1300°C. Therefore, ball milling treatment enhances the growth of 1D ZnO nanostructures but further investigation is needed to clarify the detailed role of the ball milling, as well as to induce mass transformation from nanoparticles into nanowires in solid state.

5. CONCLUSION

ZnO nanowires have been synthesized on Si wafer by heating of ZnO powders at 1300°C in Ar gas flow. The starting ZnO was prepared by ball milling of Zn powder in oxygen gas at room temperature. Ball milling induced oxidation converts Zn into ZnO with small crystalline grains. Heating at lower temperatures does not transform ZnO nanoparticles into nanowires probably due to the failure of Ge catalysts as XRD analysis suggests that 3D crystal growth occurs during heating instead of 1D growth. The enhancing effect of high energy ball milling on the nanowire growth is observed but further research is required to realize large quantity production.

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