Efficient production of ZnO nanowires by a ball milling and annealing method

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Abstract

ZnO powder was mechanically milled in a ball mill. This procedure was found to greatly increase its evaporation ability. The anomalous evaporation behaviour was caused by the disordered structure of the milled material and was not related to the increase in its surface area after milling. ZnO nanowires were synthesized by evaporation of this milled precursor. Nanowires with smooth and rough surfaces were present in the sample; the latter morphology was dominant. A green emission band centred at 510 nm was dominant in the cathodoluminescence spectrum of the nanowires.

1. Introduction

Nanowires of various materials attract a great deal of attention nowadays. This kind of nanostructure can be defined as that with only one dimension exceeding 100 nm. Unlike nanotubes, they do not have a hollow channel and represent solid crystals elongated in one direction. The most common synthesis methods for nanowire production are thermal evaporation, chemical vapour deposition, electrodeposition and solution methods [1, 2]. However, these methods are not normally able to produce large quantities of material. The increasing interest in nanowires requires the development of more efficient methods for their growth.

The ball milling and annealing method has been shown to be successful for the production of large amounts of nanotubes [3] and nanorods [4] and enhancement of the growth of nanowires by conventional thermal evaporation [5] and carbon nanotubes by pyrolysis of iron phthalocyanine [6]. High-energy ball milling is a versatile technique for the production of a range of metastable materials including supersaturated solid solutions, amorphous alloys, disordered intermetallics and quasicrystals [7]. Ball milling can also induce chemical reactions that do not normally happen at room temperature [8]. In a ball milling procedure, a reasonable amount of powder and several balls (acting as grinding media) are placed in the grinding vial. The vial is shaken or rotated in order to introduce

a high kinetic energy into the balls. The transformations of the powder happen when the balls collide with each other or the vial surface trapping some powder particles between the interacting grinding surfaces. In the ball milling and annealing method, the milled powders transform into nanowires or nanotubes upon subsequent annealing. This transformation involves solid-state processes [9] or vapour generation and deposition [5, 10, 11].

Chen *et al* [3, 9, 12] applied this technique to the growth of boron nitride and carbon nanotubes. In their procedure boron, boron nitride or carbon powders were mechanically milled during the first step and annealed at a high temperature afterwards. The preliminary milling creates special nucleation structures and introduces metal nanoparticles into the material. In the following annealing step nanotubes of a corresponding material grow starting from these structural inhomogeneities. A similar approach has been used to generate C₃N₄ and BN nanorods [4, 13].

A number of authors have used milled powders as vapour sources in the thermal evaporation approach, leading to an enhanced growth of nanowires in many cases. For example, only polycrystalline curled GaP nanowires were obtained by vapour transport of unmilled GaP powders [10], whereas high-quality single-crystalline nanowires were grown from milled powders under the same synthesis conditions. Ga₂O₃ nanobelts [5] and GaN nanoribbon rings [11] were obtained

from milled GaN samples evaporated at 930–940 °C. In contrast, no 1D nanostructures were grown from unmilled samples due to the insufficient evaporation ability of the initial GaN powder.

Although an enhanced growth of nanowires from milled powders has already been reported, the attention was mainly focused on the characterization of the nanomaterials. The authors assumed that milling led to stronger evaporation, but the evaporation behaviour of the milled materials was not presented and was not discussed in detail. However, detailed knowledge about the evaporation of milled materials is important for their successful application as vapour sources. In our opinion, this area requires further study. Ball milling effects can be related not only to the changes in surface area but also to structural changes in the milled materials.

Zinc oxide (ZnO) is an important semiconductor material with a wide band gap of 3.37 eV. The material has a wurtzite structure and no centre of symmetry. The atomic arrangement consists of alternating planes of tetrahedrally coordinated Zn^{2+} and O^{2-} ions stacked along the *c*-axis. Such a structure leads to a dipole moment and a spontaneous polarization along the *c*-axis. The material possesses piezoelectric properties, a wide band gap and a large excitonic binding energy (60 meV). ZnO nanowires were proposed to be used in field-effect transistors in nanoelectronics [14, 15]. They have been shown to be efficient nanoscale lasers [16] and can be used as light sources, waveguides [17] and optical switches [18]. Such a material has a large surface to volume ratio and can be used in semiconducting sensors [19, 20]. A number of synthetic methods have been successfully used for the growth of ZnO nanowires and special attention has been given to the thermal evaporation approach due to its simplicity and the possibility to grow a variety of nanowire-related morphologies. A review on the growth of ZnO nanostructures by thermal evaporation can be found in papers by Wang *et al* [21, 22]

In this study, we use a ball milling and annealing method for the production of ZnO nanowires by evaporation of a mechanically milled ZnO powder. The ball milling effect is carefully investigated. The significant changes in the evaporation behaviour of the milled sample are shown. The contribution of surface area and defects to the enhanced evaporation of the milled material is discussed. The structure, morphologies and luminescent properties of nanowires are analysed.

2. Experimental details

Commercial ZnO powder (Ajax Chemicals, 99.5% purity) was used as a starting material for milling. The powder was milled in a nitrogen atmosphere (excessive gas pressure of 100 kPa to prevent air contamination) in a steel magneto-ball mill for 100 h at room temperature. A description of this type of mill can be found elsewhere [23, 24]. Three grams of the ZnO powder were loaded inside the mill and four hardened steel balls (diameter of 25.4 mm) were used as a milling media. The magnet was located at the bottom of the mill at a 45° position in relation to the vertical direction. The mill was rotating around a horizontal axis at a speed of 160 rpm.

Milled ZnO powder was used to grow ZnO nanowires by a thermal evaporation process. The growth of nanostructures

Figure 1. XRD patterns of unmilled (a) and milled (b) ZnO powders.

was conducted according to the following procedure. The vapour source (milled powder) was placed at the centre of a conventional horizontal tube furnace at around 1300 °C. Ar gas flow (0.4 l min^{-1}) was used as a carrier gas to transfer ZnO vapour from the hot zone to a cooler zone of the furnace for deposition. Several Si substrates (N-type, (100) surface orientation) were located downstream and used for vapour deposition in a lower temperature zone. For determination of evaporation patterns of milled and unmilled samples, the weight losses of the vapour source materials at the above conditions were measured after heating for 1, 2.5 and 4 h. Three hundred milligrams of the powders were used as a vapour source in each experiment.

Milled ZnO powders and as-grown products were comprehensively characterized by x-ray diffraction (XRD, Philips analytical x-ray spectrometer with Co radiation $\lambda = 0.1789 \text{ nm}$), scanning electron microscopy (SEM, Hitachi S-4500, JEOL JSM6400 instruments equipped with energy-dispersive spectroscopy (EDS)), cathodoluminescence (CL) spectroscopy (Hitachi S2250-N SEM) and transmission electron microscopy (TEM, Philips CM300 and FEI F30 instrument). The surface area of both the milled and unmilled ZnO powders was measured using a Micromeritics Gemini V series surface area analyser.

3. Results and discussion

3.1. Milling effect

XRD patterns of initial and milled ZnO powders are presented in figure 1. Sharp diffraction peaks of ZnO with a wurtzite structure are seen clearly for the initial ZnO powder. In contrast, weak and broadened diffraction peaks can be seen in the pattern for the milled ZnO powders, indicating a disordered crystalline structure and small grain size. Such peak broadening is a typical feature for ball milled powders in many materials. EDS analyses of ZnO precursors and milled ZnO powders reveal that impurities were introduced into the ZnO powders during the milling process. Specifically, the impurities contain about 6.7 wt% Fe, 1.3 wt% Cr, and a negligible amount

Figure 2. Evaporation behaviour of unmilled ($\square$) and milled ($\blacksquare$) powders.

of Ni. These elements appeared in the milled sample as milling contamination from the milling container and media.

To compare the evaporation patterns of different vapour sources, a series of experiments was conducted and the weight losses of two ZnO powders at 1300 °C in Ar flow after different periods of time were measured. As can be seen from figure 2, the evaporation rate of the unmilled vapour source remains constant as its graph of weight loss is close to a straight line with time. However, this is not the case for the milled vapour source. The evaporation rate for the milled vapour source is fast in the beginning of the evaporation (the first hour) and becomes slow after 1 h of heat treatment under Ar flow at 1300 °C. Specifically, during the first 1 h heat treatment, the milled sample loses 17 wt%, whereas the unmilled sample loses only 5 wt%. The fact that the two plots have a similar slope after the first hour of heat treatment indicates that they have a similar evaporation rate. This suggests that the evaporation rate of the milled vapour source is much faster in the beginning (the first hour) and becomes similar to that of unmilled powder afterwards. After 2.5 h of annealing, the rate of evaporation from the milled material becomes even slightly lower.

As ball milling is well known as a traditional technique for reducing particle size, the increase in the surface area could be suggested as a possible explanation of the evaporation behaviour of milled ZnO powders. However, the surface area can even decrease slightly during milling in some cases. This is because, under the action of the colliding balls during milling, two processes are competing: particle fracturing and cold welding. Depending on the mechanical properties of a particular material, the former or latter can dominate leading to particle size refinement or increase, respectively [25]. In addition, the idea of a higher surface area does not explain dramatic changes in the evaporation rate of the milled vapour source with time. Apart from influencing the size of the particles, ball milling could induce various defects and reduces the grain size of the powder. Therefore, an alternative explanation of the evaporation behaviour of milled powders could be the partial disordering of the material caused by the milling treatment.

To clarify the reason for the enhanced evaporation of the milled powders, we conducted BET surface area measurements for the unmilled ZnO powder and ZnO powders milled for 50 and 100 h. Table 1 shows that the surface area is about

Table 1. Surface area of ZnO powders milled for various times.

Milling time (h)	Surface area ($\text{m}^2 \text{g}^{-1}$)
0	4
50	3.9
100	3.3

3–4 $\text{m}^2 \text{g}^{-1}$ for all samples and depends very weakly on the milling time. The surface area even decreases slightly to 3.3 $\text{m}^2 \text{g}^{-1}$ after 100 h of milling. Such a behaviour can be explained by the particle size and mechanical properties of ZnO powder. Unlike Zn and other metals, ZnO is not a ductile material, so refinement of particle sizes during milling is possible. However, there exists a critical particle size (called the limit of comminution) corresponding to the smallest possible size of particle that can be achieved by grinding [7]. If the particles are too small, they behave like a ductile material and tend to agglomerate. According to SEM analysis, the particle size in the ZnO precursors is smaller than 1 μm . We anticipate that this size is close to the equilibrium particle size for ZnO. During milling, the processes of cold welding and fracturing were nearly balanced, resulting in no significant change in the surface area. Moreover, a slight increase in the particle size possibly occurred.

Therefore, the evaporation behaviour of milled ZnO powders should be attributed to the partial disordering of the ZnO crystal structure during the milling. After milling for 100 h, the ZnO powder contains small grains, and a high density of lattice defects and grain boundaries. The presence of these imperfections accelerates vapour generation significantly in the beginning of the heat treatment. The weakly bonded atoms of the nanosized grains and those located in the grain boundaries are first vaporized rapidly. After a certain period of annealing time, the material reorganizes into crystals with a well defined crystalline structure and a limited number of residual defects. Crystals with an improved structure due to defect annihilation by structural reorganization are left. At that stage, the evaporation rate is governed by the surface area of the ZnO powders, which is similar to that of the unmilled ZnO powder. The evaporation rate becomes comparable for both samples and may become even smaller for the milled sample due to its slightly lower surface area (table 1). Indeed, figure 2 shows that the difference in weight loss between milled and unmilled vapour sources decreases slightly after 2.5 h of annealing. This simple model can convincingly explain the evolution of evaporation ability of milled ZnO powders, which is very high in the beginning and comparable with that of ZnO precursor after the first hour of annealing.

3.2. Characterization of ZnO nanowires

As can be noted above, 1 h is the time of anomalously enhanced evaporation from the milled ZnO powders. As a consequence, we chose 1 h to be the standard synthesis time for growing ZnO nanowires by evaporating milled ZnO powders. According to SEM and TEM investigations, a layer of nanowires was formed on the Si substrates located at a temperature zone of approximately 250–400 °C (at a distance of 17–20 cm from the vapour source).

Figure 3. SEM images of ZnO nanowires. (a) Low magnification image of a nanowire layer. (b) A typical nanowire. (c) Branches of nanowires.

Figure 3 shows a typical SEM image of a nanowire layer. The nanowires cover a large surface area of the substrate with a high density. The diameter of the nanowires is typically between 20 and 80 nm with the length up to tens of micrometres. The general morphology of the nanowires is the same, but the diameter of the nanowires is a function of the distance from the vapour source. Thinner nanowires form in more distant areas where the temperature is lower. No catalytic particles, typically required for the vapour–liquid–solid growth mechanism [26], were observed at the nanowire tips. The SEM image in figure 3(b) shows the typical morphology of a nanowire. Branches developed from parent nanowires can often be observed. Figure 3(c) shows such an example. The crystal structure and composition of the ZnO nanowires obtained was confirmed by XRD and EDS analyses. EDS analysis did not reveal the presence of Fe, Cr or Ni in the sample, suggesting that these elements present as contaminants in the vapour source do not participate in vapour transport to the location of the ZnO nanowires.

Figure 4 shows TEM images of ZnO nanowires. The general morphology of nanowires is shown in figure 4(a). Generally, these nanowires can be attributed to two basic types, namely nanowires with a smooth surface (figure 4(b)) and nanowires with a rough surface (figure 4(c)). The number of nanowires with a rough surface is larger. We speculate that the surface of such nanowires is built mainly with some

preferential facets. However, the determination of these facets requires further work and is not presented here. In most cases reported in the literature, ZnO nanowires grow with smooth side surfaces along the $\langle 0001 \rangle$, $\langle 10\bar{1}0 \rangle$ or $\langle 11\bar{2}0 \rangle$ directions [27] and the type of faceting reported here is a rather unusual phenomenon for ZnO.

As was mentioned above, the branching of wires can often be observed in the sample. Long nanowires can join together or some shorter ZnO rods can be found on the surface of the parent nanowire. Our TEM analysis showed that all of the connections between branches and nanowires form a single-crystalline body. Figure 4(d) presents one of the connections between the nanowires. The high-resolution TEM image of the enlarged fragment of this connection area is shown in figure 4(e). According to the diffraction pattern (figure 4(f)), a nanowire with a rough surface grows along the $[0001]$ direction, whereas a nanowire with a smooth surface grows along the $[01\bar{1}0]$ direction. It can often be observed that a nanowire with a rough surface has smooth branches or vice versa. However, this general rule has exceptions.

Figure 5 shows cathodoluminescence spectra of ZnO nanowires and a stoichiometric ZnO powder (Alfa Aesar). The CL spectrum of the ZnO powder shows a near-band-edge (NBE) peak centred at 390 nm (3.19 eV), which is attributed to bound and free exciton emissions [28]. The NBE emission is hardly observable in the CL spectrum of the ZnO nanowires. Piqueras *et al* suggested that this CL quenching is due to defects in the zinc sublattice, possibly vacancies acting as electron traps [29]. Such a strong suppression of the NBE peak is not usually observed in ZnO nanowires grown by other methods [30].

A wide green emission band centred at 510 nm (2.43 eV) dominates the CL spectrum of the nanowires. This emission band is quite typical for ZnO materials but its origin is still controversial. It is conventionally attributed to singly ionized oxygen vacancies [31] but different origins such as zinc vacancies [32], interstitial zinc ions [33], copper impurities [34] and others have also been proposed. van Dijken *et al* [35, 36] explained this emission by a transition of an electron from a level close to the conduction band edge to a deeply trapped hole Vo^{**} in the bulk of the ZnO particle. The Vo^{**} centres were generated by surface trapping of photogenerated holes, followed by their transfer from the valence band to Vo^* levels in the bulk. It is also possible that the green emission was enhanced by impurities such as Fe, Cr and Ni. Indeed, these impurities were present in the milled material used as a vapour source. However, we did not find any evidence of the presence of these elements in the nanowires by EDS and TEM analysis and we believe that they do not participate in the vapour transport and stay in the vapour source material because of the high melting points. Therefore, we believe that Fe, Cr and Ni impurities do not contribute to the detectable luminescent properties of ZnO nanowires. Regardless of the origin of the emission band, it can be a merit that the ZnO nanowires grown via the ball-milling and annealing method exhibit a dominant green emission. Such enhancement of a particular emission band is important for the applications of ZnO nanowires as a luminescent material.

Figure 4. TEM images of ZnO nanowires. (a) Low resolution bright-field image. (b), (c) Nanowires with a smooth and rough surface, respectively. (d) Low resolution image of a connection area between two nanowires. (e) High resolution image of the area marked with a square in (d). (f) Selected area diffraction pattern of the connection area of the nanowires shown in (d) and (e).

Figure 5. CL spectra of ZnO nanowires and ZnO powder taken at the accelerating voltage of 15 kV and emission current of 30 μ A.

4. Conclusions

Ball milling of ZnO powder greatly enhances its evaporation ability. The observed anomalous behaviour of the milled material is not related to a larger surface area but is defined by a partially disordered structure induced by ball milling. ZnO nanowires were synthesized by evaporation of the milled powder. Nanowires with rough and smooth surfaces coexist in the sample and the former morphology is dominant. The cathodoluminescence spectrum of the nanowires shows a dominant green emission band.

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