Powder Technology 319 (2017) 204–209

Contents lists available at ScienceDirect

Powder Technology

journal homepage: www.elsevier.com/locate/powtec

Structured zinc oxide powder materials: Synthesis and further investigations of their thermal morphological stability

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ARTICLE INFO

Article history:
Received 9 June 2016
Received in revised form 17 April 2017
Accepted 14 June 2017
Available online 16 June 2017

Keywords:
Zinc oxide
Rod
Star
Aqueous
Morphology
Annealing
Structured particles

ABSTRACT

ZnO is a versatile metal oxide with a wide range of applications in optoelectronics, catalysis, medicine and lightweight technology. Recently, two powder crystalline structures of ZnO were produced from an aqueous amine-containing zinc salt solution in a 30 to 120 min reaction under atmospheric pressure. The novelty concerns the synthesis of the particles. Such particles have been produced in a low temperature synthesis under atmospheric conditions and the synthesis route follows not the conventional hydrothermal route in an autoclave, but in an open vessel. Nevertheless, it is possible to produce particles with a specific structure and small size distribution. On the one hand, rod-like particles with a size up to 1.5 μm in length and 0.3 μm in width and on the other hand star-like particles with a size up to 0.7 μm in diameter and branches <0.3 μm were produced. The identification was carried out by means of Raman spectroscopy, the morphology by scanning electron microscopy, and its crystallinity by means of X-ray diffractometry. To explain the structure formation, we developed schematically the formation mechanism starting from a zinc embryo. To improve the suitability of these materials in composite materials, e.g., as an additive in sintered metals or in foundry processes, these structures were further exposed in a 2 h annealing process from 500 °C to 900 °C. The effects on morphology and crystal size are investigated by FE-SEM and XRD-measurements. In both cases, aluminum and magnesium are suitable candidates as matrix material since they have their melting points in the above-mentioned temperature interval. In addition to the chemical resistance, the stability of the particles at these temperatures is a major factor in the first testing. The star-like shaped particles showed a temperature resistance of up to 500 °C, and the rod-like shaped particles even up to 700 °C, confirming the possibility of use in the above mentioned applications.

1. Introduction

There is an increasing scientific interest concerning zinc oxide in research, extensively studied in scientific fields like solar cell technology [1,2], photo catalysis [3,4], optoelectronics [5] and sensor technique [6,7], as well as biotechnology [8,9].

As II–VI semiconductor with a wide band gap of 3.37 eV at 300 K and a large exciton binding energy of 60 meV in bulk, ZnO enables various optoelectronic applications [10]. Due to its thermodynamic stable crystal structure, wurtzite type, it is an interesting thin film system at the nano level. Its attractiveness can be attributed to the high surface-to-volume ratio.

Meanwhile, there are numerous preparation methods to synthesize nanosized zinc oxide, especially the hydrothermal synthesis route and aqueous chemical growth thin film processing technique (ACG) [11,12].

Lionel Vayssieres developed the concept of a substrate specific thin film growth in order to produce a highly oriented metal oxide nanorod-array. Vayssieres worked with an aqueous medium and temperatures under 100 °C. This technique allows the control of the thin film particle shape, orientation and size, which enables the fabrication of a large scale of metal oxides like α-Cr_2O_3, α-Fe_2O_3, γ-MnOOH, ZnO on different substrates [13].

The scope of this work was the fabrication of structured ZnO powder materials followed by a thermal stability study of the morphology by SEM and Raman spectroscopy [13].

1.1. Aqueous chemical growth process (ACG) to produce ZnO

The growth ZnO is described by the following equations. Eq. (1) shows the noncyclic tertiary amine HMTA ($C_6H_{12}N_4$), which hydrolyze in water to produce formaldehyde (HCHO) and ammonia (NH_3) [13] [14].

$$C_6H_{12}N_4 + 6\ H_2O \leftrightarrow 4\ NH_3 + 6\ HCHO \quad (1)$$

In solution, the ammonia (NH_3) oxidizes to ammonium ions (NH_4^+), as seen in Eq. (2), and reduces the water molecules to hydroxide ions (OH^-) [14].

$$NH_3 + H_2O \leftrightarrow NH_4^+ + OH^- \quad (2)$$

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http://dx.doi.org/10.1016/j.powtec.2017.06.031
0032-5910/

In aqueous solution, Zn^{2+} cations coordinate the ammonium anions to form the $[Zn(NH_3)_4]^{2+}$ a tetrammine zinc(II) complex (Eq. (3)) [14].

$$Zn^{2+} + 4\ NH_3 \leftrightarrow [Zn(NH_3)_4]^{2+} \quad (3)$$

The residual Zn^{2+} coordinates two hydroxide ions to form zinc hydroxide, which reacts to zinc oxide (ZnO) and water, which is shown in Eqs. (4) and (5) [14].

$$Zn^{2+} + 2\ OH^- \leftrightarrow Zn(OH)_2 \quad (4)$$

$$Zn(OH)_2 \leftrightarrow ZnO + H_2O \quad (5)$$

Without any additives the crystal growth takes place, preferably along the polar plane of the wurtzite cell. Its polar planes {0 0 0 1} and {0 0 0 -1} have a higher surface energy than the nonpolar planes {1010} and {1 0 -1 0}, which results in the rod-like shaped zinc oxide [14].

1.2. Raman activity of ZnO

The optical phonons of ZnO at the Γ point of the Brillouin zone is in accordance with the irreducible representation: [10,15,16].

$$\Gamma = A_1 + E_1 + 2E_2 + 2B_1 \quad (6)$$

In Eq. (6) the polar modes A_1 and E_1 are infrared and Raman active and split into transversal (TO) and longitudinal (LO) optical phonons. The splitting in TO and LO phonons is due to the electrical field in a crystal structure. The B_1 mode is neither infrared nor Raman inactive and is called the silent mode. The mode E_2 is non-polar and Raman active. In Table 1, the frequencies of the optical phonon modes of zinc oxide are summarized. The scattering geometry is expressed by the Raman-selection rule [15–18].

2. Material and methods

All vessels and used materials were cleaned in an RCA (Radio Cooperation of America)-solution containing deionized water, ammonia (NH_3, 25%) and hydrogen peroxide (H_2O_2, 35%) in a ratio 5:1:1. All syntheses are reproducible if the synthesis instructions are followed.

2.1. Synthesis strategies

2.1.1. Synthesis of rod-like shaped particles

To fabricate rod-like ZnO crystals, a precursor solution containing 0.025 M zinc nitrate hexahydrate (Roth, ≥99% p.a.) and 0.025 M hexamethylenetetramine (Roth, ≥99% p.a.) was prepared using deionized water. The precursor solution was filled into a screw-top-bottle (DURAN®, Roth) and was immediately placed in a 97 °C hot water bath which was wrapped with aluminum foil. The processing was performed at 90 °C for 30 min. Thereafter, the hot solution with its white powder was filtered by a glass suction filter G4 (VWR International GmbH, Darmstadt) and a qualitative paper filter with a particle retention of 2 μm. Finally the powder material was dried at 60 °C in an oven.

Table 1
The frequencies of optical phonon modes of zinc oxide at Γ point of the Brillouin zone [15–18].

Mode	Frequencies in cm^{-1}	Selection rule
E_2^{low}	101	$y(xx)\bar{y}, z(xx)\bar{z}, z(xx)\bar{z}$
B_1^{low}	260	Silent mode
A_1(TO)	380	$y(xx)\bar{y}$, $y(zz)\bar{y}$
E_1(TO)	407	$y(zx)\bar{y}$
E_2^{high}	437	$y(xx)\bar{y}$, $z(xy)\bar{z}$, $z(xx)\bar{z}$
B_1^{high}	550	Silent mode
A_1(LO)	474	$z(xx)\bar{z}$
E_1(LO)	583	Not in backscatter geometry

2.1.2. Synthesis of star-like shaped particles

To fabricate star-like ZnO crystals, a precursor solution was prepared as mentioned above. The solution was filled in an open glass beaker (DURAN®, Roth) and set into a 60 °C hot water bath for 120 min and was cooled down at room temperature afterwards. The beaker was closed by an aluminum foil wrapped ceramic plate. Thereafter, the "cold" (RT) solution with its white powder was filtered (like mentioned above) and dried at 60 °C in an oven.

2.2. Annealing process

To evaluate the thermal morphological stability, an incinerating furnace (Carbolite Gero GmBH & Co. KG, Neuhausen, Germany) was used. Crucibles were filled with 0.2 g of the as synthesized powder material. The heat treatment was performed at 500 °C, 700 °C and 900 °C and heated at 5 °C per minute to the appropriate temperature.

2.3. Characterization methods

2.3.1. Scanning electron microscopy

The morphology of the as prepared and annealed powder material was characterized by means of FE-SEM (ZEISS ULTRA PLUS (Carl Zeiss SMTAG, Oberkochen, Germany)) at an accelerating voltage of 2.0 kV and 20 kV.

2.3.2. Powder X-ray diffractometry

Wide-angle X-ray diffraction measurements were done with the Diffractometer X'Pert Phillips (now PANalytical GmbH) with a Cu anode in a 2Θ angle range between 20° and 80°.

2.3.3. Raman spectroscopy

Raman spectroscopy measurements were performed with an InVia Renishaw Raman microscope (Renishaw plc, United Kingdom). The Raman spectra were excited by a 532 nm YAG-laser with a power of 50 mW, 1800 l/mm gratings and a 50× objective.

3. Results and discussion

3.1. Two particle morphologies

The rod-like and star-like crystal growth is presented in Fig. 1. In both cases, ZnO embryos were formed and grew preferably along the polar planes {0 0 0 1} and {0 0 0 -1} of wurtzite type cell structure. In case of the star-like shaped powder material more branches arise from the ZnO embryo due to the lower temperature, which results in the star-like shape. The FE-SEM images in Figs. 2, 3 and 4 confirms this behavior. Due to the fast expansion of the rod-like shape in {0 0 0 1} and {0 0 0 -1} direction, there is a tendency to form a pore from the center of the body which extends along these above mentioned directions too (see Fig. 3 (Id.)). The obtained as-prepared ZnO rod-like and star-like shaped particles fabricated under different reaction conditions exhibit the hexagonal wurtzite structure that was revealed by X-ray-diffraction in Fig. 2 and which can be indexed to the standard spectrum of the ICSD database No. 57-450. The lower peak intensities observed in the diffraction profile of rod-like crystals (a) compared with the profile of star-like crystals (b) could be caused by the different particle size and morphology.