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Anomalous coarsening of nanocrystalline zinc oxide particles in humid air

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ABSTRACT

Zinc acetate in combination with water plays a key role during the coarsening of zinc oxide (ZnO) nanocrystals at moderate temperature (85 °C) in air. The growth of ZnO nanocrystals is well known in liquid phase systems, but this work shows that this process is strongly enhanced in powder form by the presence of residual acetate. The growth of the ZnO nanocrystals was documented by X-ray diffraction (XRD) and high resolution transmission electron microscopy (HRTEM), showing a preferred growth along [0001] crystallographic direction. An increase of more than 400% in crystal size was observed, which could be related to coarsening but not due to precipitation from solution. In contrast, particle size stayed almost constant if pure zinc oxide powder was used. This growth is expected to slowly occur during storage even under ambient conditions. The limited stability of nanopowders limits their applicability as well as pressing into bulk materials.

1. Introduction

Zinc oxide (ZnO) is a *n*-type semiconductor that is extensively used in electronic and optoelectronic systems due to its combination of electrical properties, such as wide band gap of 3.37 eV and a large exciton binding energy of 60 mV. In general, the novel electrical and optical properties of nanostructured ZnO have positioned this material as one of the most promising ceramics for the new generation of devices such as gas sensors, varistors, lasers, diodes, ultraviolet detectors, solar cells and nanogenerators for self-powered systems, as well as for biological cell labeling [1–6].

Nevertheless, the understanding of mechanisms involved in the coarsening of nanocrystalline ZnO is required as excessive coarsening could entail decrease of final properties and functionalities. In the present work, coarsening of zinc oxide nanocrystals was observed during exposure under humidified air and temperatures up to 85 °C. Coarsening of nanopowders during storage is an undesirable effect, as typical applications require maintaining a small initial crystal size. It is commonly assumed that ZnO is chemically stable at standard ambient conditions of temperature and pressure. However, ZnO crystals in the nanometer scale seem to be sensitive to the environment. Ali and Winterer [7] reported the coarsening of nanocrystalline ZnO particles in ambient atmosphere. This increase in crystal size was explained by the interaction of ambient water with the surface of the ZnO particles causing the formation of crystal defects. In contrast to typical growth environment, the coarsening of their ZnO particles was not investigated in liquid solution but in powder form. Here, untypical coarsening is observed without the presence of reactants or elevated temperature. Further, it was suggested that the mass transport is caused by enhanced diffusivity due to interaction of ZnO crystal defects with dissociated water species. The suggested growth model by Ali and Winterer is not taking into account any preferred crystalline growth direction. ZnO crystals exhibit several growth patterns and may form films [8,9], spheres [10], whiskers [11], rods [12] and flower-like particles [13] depending on the synthesis conditions. This manifold growth behavior is based on the polar nature of the crystal with preferred growth along the polar *c*-axis of the ZnO crystal [14]. Finally, the observed crystal growth kinetics differs in the classical growth models which describe a liquid phase model.

2. Experimental procedure

The commercially purchased ZnO powder used for the experiments is referred as ZinCox10 (IBU-tec advanced materials AG, Weimar, Germany) with a purity of >99.00 wt%. The manufacturer datasheet announces that the powder is composed of spherical particles with a mean particle size (d_{50}) of 10 ± 3 nm and a specific surface area of 60 ± 5 m^2/g (measured by BET). An additional ZnO powder (NG20, Nanogate AG, Quierschied-Göttelborn, Germany) with a purity of >99.99 wt% and $d_{50}=32.9$ nm was used as reference

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powder. At the beginning both powders were characterized as received. The particle size distributions were measured by means of transmission electron microscopy (TEM) and X-ray diffraction (XRD). TEM was performed with a JEM-3010 (JEOL, Akishima, Japan) operated at 300 kV. The powder specimens were prepared by dispersing the powder in ethanol and a drop of this diluted suspension was placed onto a copper carbon grid. A minimum of 200 particles were measured to obtain size distribution, mean particle diameter and standard deviation. The length and width of each particle was measured, so that the aspect ratio (ratio of length to width) could be computed for each particle. The size distributions were obtained by classification of length, width and aspect ratio values. XRD measurement was carried out using a D8-Discover (Bruker AXS, Billerica, USA) with Cu-K$_\alpha$ radiation at $\lambda = 1.54056$ Å, operated at 40 kV and 40 mA, a step size of 0.02° and a counting time of 1.6 s. The determination of the crystallite sizes was performed by fitting the $(10\overline{1}0)$, $(11\overline{2}0)$ and (0002) Bragg peaks by Scherrer analysis by means of the pseudovoigt function. A shape factor $K = 0.94$ was applied for Scherrer equation [15] and full width half-maximum was corrected in respect to instrumental broadening. Further details on refinement are explained elsewhere [16]. Furthermore, X-ray photoelectron spectroscopy (XPS) was carried out at the ZinCox10 powder by a Quantum 2000 (Physical Electronics Inc., Minnesota, USA) with a residual gas pressure of 2×10^{-9} Torr. The spectra were obtained using an Al K$_\alpha$ X-ray source ($h\nu = 1438$ eV) and an angle of 45° to determine the state of binding energies for zinc, oxygen, carbon and nitrogen. The background of the spectrum was fitted with a Shirley function. The amount of carbon and nitrogen of the ZinCox10 powder was measured by a carbon–nitrogen–sulfur analyzer (Vario EL Cube, Elementar Analysesysteme GmbH, Hanau, Germany) which was calibrated by means of sulfanilic acid and a thermal conductivity detector composed of tungsten.

0.4 g of ZnO powder was stored in a glass beaker inside an environmental chamber (KBF 240, Binder GmbH, Tuttlingen, Germany) under temperatures between 20 °C and 85 °C and in moistures between 1.0 g/m^3 and 140 g/m^3. In particular, 85 °C with 140 g/m^3 (40% relative humidity) and 20 °C with 14 g/m^3 (85% relative humidity) will be further referred to "humid warm" and "humid cold" conditions, respectively. In comparison, ZnO powder was stored in a drying cabinet at 105 °C with < 0.5 g/m^3 (< 0.1% relative humidity) and will further be referred to "hot" condition. The ZnO powders were then stored for 1 h, 24 h and 168 h (7 days) under defined environmental conditions as mentioned above and characterized afterwards with respect to particle size. The dimensions of the grown particles were correlated with their crystallographic orientation by two methods. First, the mean particle sizes obtained from Bragg peaks were related to the crystallographic orientation of the particles. The second method relied on TEM measurements of particles after a storage time of 168 h at 85 °C and 140 g/m^3 moisture. In addition the distances between the lattice fringes of several orientated particles were identified and directly correlated with the particle dimensions. These results were supported by a nano-beam diffraction method on selected particles [17]. Fourier-transform infrared spectroscopy (FTIR) measurements were carried out with an Alpha spectrometer (Bruker Optics, Billerica, USA) using an absolute total reflection method. Each measurement was performed twice with approximately 20 mg powder and a resolution of 4 cm^{-1}. Zinc acetate dihydrate Zn(H$_3$C$-$COO)$_2$ (Sigma-Aldrich, St. Louis, USA) with a purity of >99% was analyzed by FTIR as reference.

3. Results

3.1. Characterization of as received ZnO powder

TEM observation reveals polyhedral, nearly spherical particle shape for both ZnO powders as they were received from the producers (Fig. 1(a)–(b)). The corresponding crystal size distributions are shown below the TEM images. Table 1 lists the median values of width, length and aspect ratio for the standard fine powder (ZinCox10) and the high

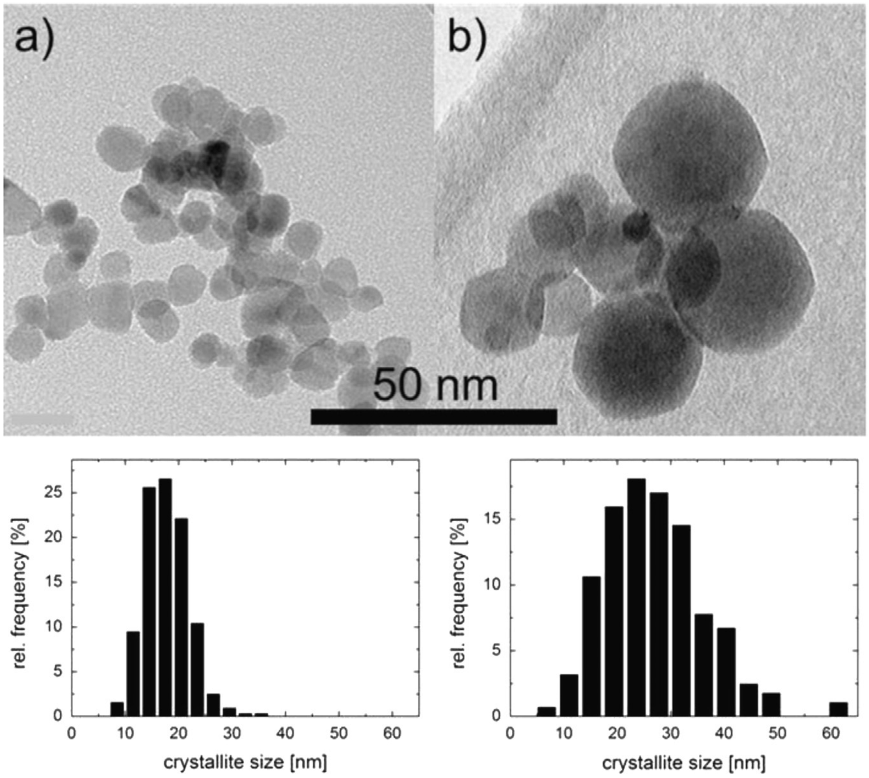

Fig. 1. TEM images of as received powder: (a) ZinCox10 and (b) NG20. Corresponding crystal size distributions are shown.