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Three-Dimensional Array of Highly Oriented Crystalline ZnO Microtubes

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The control of the shape and the orientation of nano-/microcrystallites as well as the ability to order and align them into large three-dimensional arrays onto various types of substrates represent essential tasks to fulfill to create the future generation of smart and functional particulate thin film materials. In addition, numerous applications require a high porosity and large surface area to fulfill the demand of high efficiency and activity. For instance, dye-sensitized photovoltaic cells, dimensionally stable anodes (DSA), metal-ion batteries, electrochemical supercapacitors, hydrogen storage devices, and bio- and gas sensors require the development of new functional porous materials to achieve better and optimized performances. Decreasing the particle size is one effective way to greatly increase the specific surface area of materials. Alternatively, one may design materials with hollow structures to contribute simultaneously to the extension of porosity and surface area. Novel devices, with a higher level of engineering combining hollow and oriented structures providing enhanced and smart functionality, may therefore be created to fulfill the requirement of high technological applications. Several classes of materials (insulator, semiconductor, metallic, and magnetic) have been synthesized with tubular micro/nano hollow texture such as SiO_2,[1] TiO_2,[2] InGaAs/GaAs,[3] WS_2,[4] MoS_2,[5] NbS_2,[6] $Na_2V_3O_7$,[7] V_2O_5,[8] VO_x,[9] BN,[10] and carbon nanotubes.[11,12] The current synthetic techniques to produce aligned nano/microtubes are laser patterning,[13] replication, and template techniques[14–16] or CVD growth in a confined environment.[17] However, the economic and industrial wants and needs of low-cost thin film processing techniques for the large-scale production of materials with necessary performance and engineered surface functionality

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will most probably arise from solution chemistry. Hence, our strategy to control the shape and the orientation of crystallites in large arrays consists of growing thin films materials, directly onto substrates, without a template, from molecular scale to nano-/meso- and microscale, from aqueous precursors in solution by monitoring the thermodynamics and kinetics of nucleation and growth of the materials by controlling experimentally its interfacial tension.[18,19] A general concept, *purpose-built materials*,[20] as well as thin film processing aqueous growth method[21] have been developed and are dedicated to the novel design of metal oxides particulate thin films with controlled crystallite size, surface morphology, thin film texture, orientation, and overall porosity. Such an approach has been successfully applied to demonstrate the ability to chemically grow, align, and orientate nano-/microparticles onto substrates with an aqueous low-temperature coating process. For instance, the design of large arrays of three-dimensional crystalline highly oriented ferric oxide nanorod arrays[22] led to the development of a hematite wet photovoltaic cell.[23] Recently, a three-dimensional highly oriented hexagonal microrod array[24] of ZnO with a tailored length over an order of magnitude have also been successfully produced by the same concept and aqueous thin film processing technique. Such arrays show high photoresponse in the UV region and excellent electron transport properties over a wide range of rod lengths.[25]

Zinc oxide is an important low-cost basic II−VI semiconductor material which is used considerably for its catalytic,[26,27] electrical,[28−31] optoelectronic,[32−35] and photoelectrochemical properties.[36−38] Consequently, designing ZnO material with novel morphology and, in particular, highly porous and well-defined anisotropic and highly oriented three-dimensional arrays is of significant importance for basic fundamental research as well as of relevance for various fields of industrial and high-tech applications.

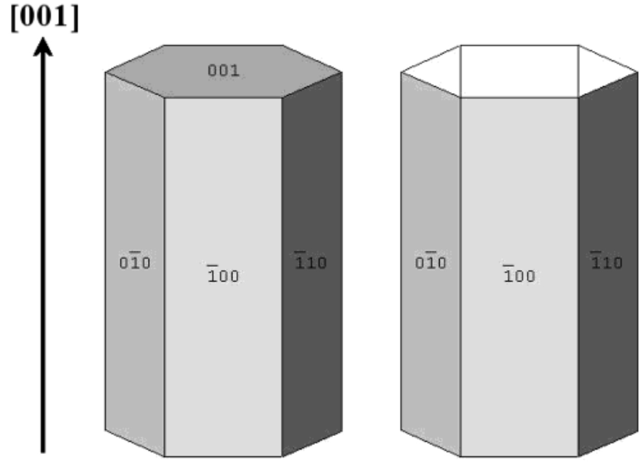

Figure 1. Crystal habit of wurtzite ZnO hexagonal rod and tube.

To comprehend the possibility to generate ZnO microtubes, one has to understand its structural characteristics. Indeed, the thermodynamically stable crystal structure of ZnO is wurtzite (hexagonal crystal system) and occurs in nature as the mineral Zincite (crystal class 6*mm*). This ionic and polar structure can be described as hexagonal close packing of oxygen and zinc atoms in space group $P6_3mc$ with zinc atoms in tetrahedral sites (point group 3*m*). The occupancy of four of the eight tetrahedral sites of the hexagonal lattice controls the structure. The typical crystal habit exhibits a basal (pedion) polar *oxygen* plane (00$\bar{1}$), a top tetrahedron corner-exposed polar *zinc* (001) face, and low-index faces (parallel to the *c* axis) consisting of a nonpolar ($\bar{1}$00) face (and C_{6v} symmetric ones). The "low-symmetry" nonpolar faces, with 3-fold coordinated atoms are the most stable ones, the polar ones being metastable. Additionally, there is no center of inversion in the wurtzite crystal structure and therefore an inherent asymmetry along the *c* axis is present which allows the anisotropic growth of the crystal along the [001] direction. The velocities of crystal growth in different directions are reported to be [$\bar{1}$00] > [$\bar{1}$01] > [001] ≈ [00$\bar{1}$].[39] Accordingly, the theoretical and most stable crystal habit is a hexagon elongated along the *c* axis (Figure 1).

The structural characteristic (asymmetry) has been used to create a three-dimensional array of a highly oriented microrod array of ZnO[24] and the structural surface metastability of the polar surface will be used in the present paper to design the corresponding hollow structure. Indeed, by playing chemically on the structural metastability of the materials and by creating a precipitation and aging medium which takes advantage of the surface metastability of the polar faces and in particular the top (001)-Zn face, one may create a highly oriented microtubular array of ZnO on various (polycrystalline or single-crystalline) substrates by a one-step, template-free, simple and cheap, aqueous synthesis. Indeed, in the early stage of the synthesis (day 1),

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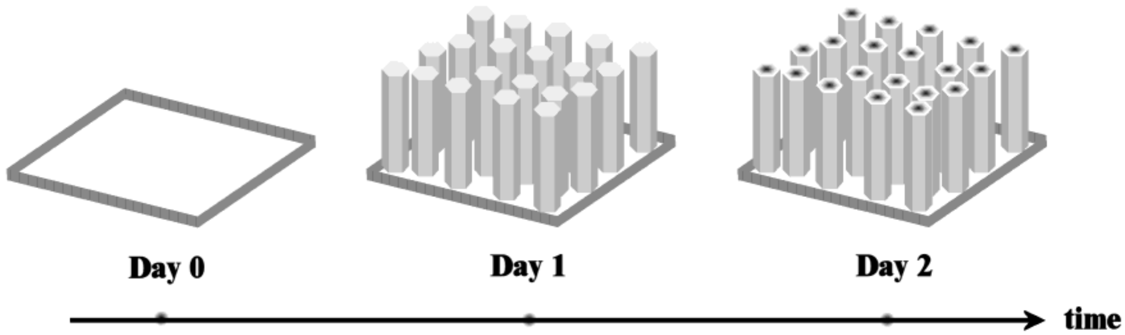

Figure 2. Scheme of solution growth of highly oriented microtubular array of ZnO onto substrates.

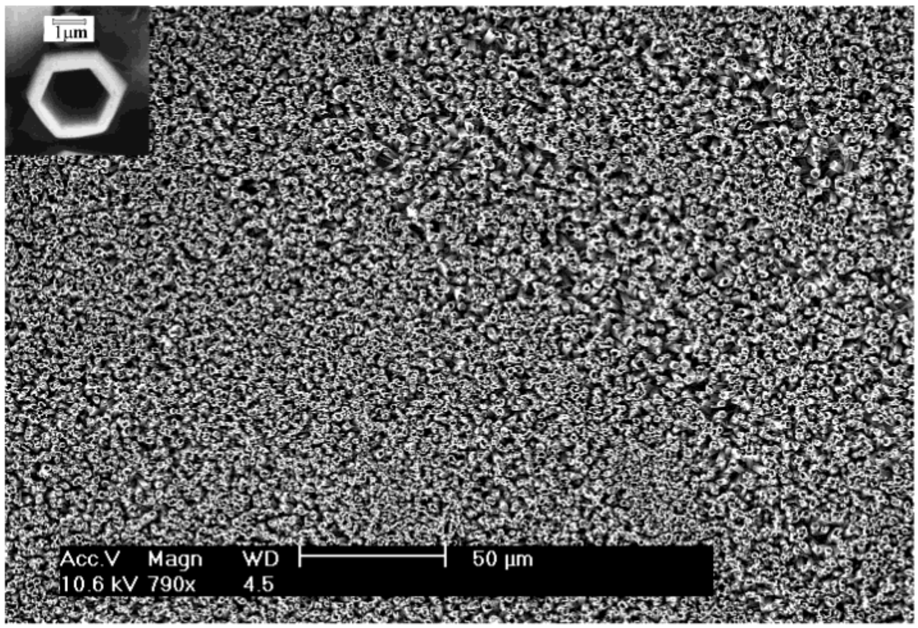

Figure 3. FEG-SEM micrographs of ZnO oriented microtube array chemically grown onto a transparent conducting oxide (TCO) glass substrate.

the nucleation and growth of the highly oriented three-dimensional crystalline zincite ZnO microrod array of typically 1−2 μm in width and up to 10 μm in length is produced as described in detail in ref 24. Subsequently, in a second stage (day 2), that is, the aging process, the preferential chemical dissolution of the metastable (001)-Zn faces of the fully grown oriented microrods shall lead to the required highly porous and oriented nonpolar hollow structure (Figure 2). The aging conditions are such that the systems will tend to reach their thermodynamic colloidal stability and may therefore undergo variations of morphology, size, or structural properties[18] as a result of the aging mechanism (e.g., Ostwald ripening).[40]

Accordingly, the synthesis was conducted by the thermal decomposition of a Zn^{2+} amino complex with reagent-grade chemicals. Methenamine, $(CH_2)_6N_4$, a nontoxic, water-soluble, nonionic tetradentate cyclic tertiary amine was chosen to comply simultaneously with the precipitation of the divalent post-transition metal ion Zn^{2+}, the nucleation growth of its stable oxide form, zincite ZnO, and the dissolution of its metastable polar face (001) by aging. An equimolar (0.1 M) aqueous solution (MilliQ+, 18.2 MΩ-cm) of zinc nitrate, $Zn(NO_3)_2{\cdot}4H_2O$, and methenamine was prepared in a bottle with an autoclavable screw cap. A polycrystalline F−SnO_2 glass substrate (e.g., Hartford Glass Inc.), silicon wafers, or ITO-coated polyester substrate, washed and cleaned with MilliQ water and spectroscopic-grade ethanol and dried under N_2 gas flow, was placed inside. The bottle is then heated at a constant temperature of 90 °C for 2 days in a regular laboratory oven. Subsequently, the homogeneous thin films are thoroughly washed with (MilliQ+) water to remove any contamination from residual salts or amino complex.

As expected, well-aligned single-crystalline hexagonal tubes of typically 1−2 μm in width (inset Figure 3) and about 10 μm in length, with well-defined crystallographic faces are grown, along the [001] direction, and oriented in a perpendicular fashion onto the substrate and arranged in very large uniform arrays (Figure 3). According to electron and X-ray diffraction, zincite (wurtzite ZnO) is the only crystallographic phase detected (Figure 4) without significant shift of the lattice spacing compared to bulk ZnO. In addition, one may notice on the indexed X-ray pattern that the texture effect observed on the microrods (highest relative intensity for the 002 line)[24] due to the orientation of the

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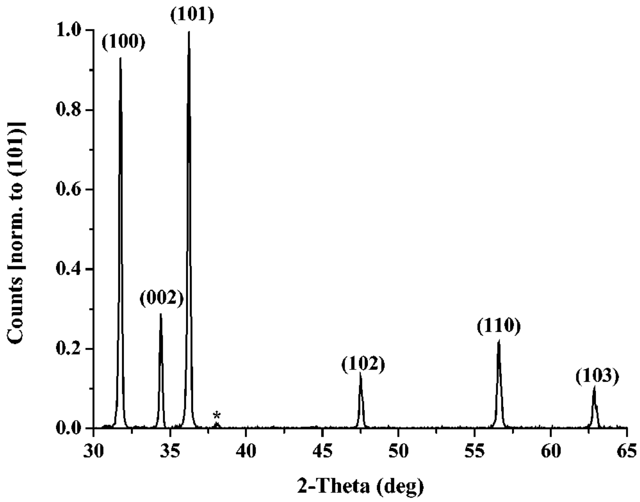

Figure 4. Indexed X-ray diffraction pattern of a highly oriented zincite ZnO microtube array grown on a F−SnO_2 substrate (*).

rods onto the substrate is not observed because the (00*n*) planes are absent in the hollow structure (Figure 1).

Given that the material is crystalline, no additional heat treatment is necessary, allowing, for instance, the use of flexible or temperature-sensitive substrates. Fully covered and uniform arrays of several tens of centimeter square, and potentially much larger with larger substrate and container, may easily be produced at very low cost and in a reasonable amount of time.

The effect of the overall concentrations (metal and metal/complex ratio) is currently under investigation to vary and control the width of the tubes, the thickness of the walls, and the overall porosity of the materials and to create highly oriented ZnO nanotubes.

The development of such a hollow array has been carried out for several applications. First, for dye-sensitized photovoltaic cells,[41,42] by combination of a high surface area/porosity and the direct oriented pathway[23] for a photogenerated electron, higher photoefficiency is foreseen. Second, such an array with its well-defined adsorption microcavities will be used to develop novel devices such as bio-/gas sensors. For instance, the adsorption of DNA, peptides, proteins, or antibodies on well-defined surfaces such as the nonpolar faces (walls) of ZnO microtubes by electrostatic or van der Waals interaction will allow the development of novel sensors as well as molecular modeling studies of their interactions on well-defined crystal faces. In addition, in view of the well-studied physical properties of ZnO[28−38] in the literature, one may develop novel amperometric, luminescent, or photoconductive sensors. Finally, such a structure will be used as a template to create three-dimensional arrays of composite materials with functional architecture at low cost and large scale by coating the ZnO microtubes with metal or semiconductor nanoparticles.

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