

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/231629739>

# Purpose-Built Anisotropic Metal Oxide Material: 3D Highly Oriented Microrod Array of ZnO

ARTICLE in THE JOURNAL OF PHYSICAL CHEMISTRY B · APRIL 2001

Impact Factor: 3.3 · DOI: 10.1021/jp010026s

CITATIONS

664

READS

458

4 AUTHORS, INCLUDING:



Lionel Vayssieres

Xi'an Jiaotong University

70 PUBLICATIONS 5,922 CITATIONS

SEE PROFILE



Sten-Eric Lindquist

86 PUBLICATIONS 8,802 CITATIONS

SEE PROFILE



Anders Hagfeldt

École Polytechnique Fédérale de Lausanne

390 PUBLICATIONS 31,903 CITATIONS

SEE PROFILE

## Purpose-Built Anisotropic Metal Oxide Material: 3D Highly Oriented Microrod Array of ZnO

Lionel Vayssieres,\* Karin Keis, Sten-Eric Lindquist, and Anders Hagfeldt

Department of Physical Chemistry, Uppsala University, Box 532, 75121 Uppsala, Sweden

Received: January 4, 2001; In Final Form: March 19, 2001

We are reporting here on the inexpensive fabrication of large three-dimensional and highly oriented porous microrod array of n-type ZnO semiconductor with a unique designed architecture consisting of well-defined, length-tailored, monodisperse, perpendicularly oriented single-crystalline hexagonal rods, grown directly onto polycrystalline, single-crystalline, or amorphous substrates, from an aqueous solution of zinc salt at low temperature.

The control of the shape and the orientation of nano-/microcrystallites as well as the ability to order them into large three-dimensional arrays onto various types of substrates represent essential tasks to fulfill in order to create a future generation of smart and functional materials. Hitherto, the competence to generate aligned and ordered crystallites onto substrates was essentially based on template/membrane synthesis,<sup>1</sup> patterning techniques,<sup>2</sup> or epitaxial electrodeposition.<sup>3</sup>

Our strategy to control the shape and orientation of crystallites consists of growing thin-film materials directly onto substrates, from the molecular scale to the nano-/mesoscale, from aqueous precursors in solution by monitoring the thermodynamics and kinetics of nucleation and growth of the materials by controlling experimentally its interfacial tension.<sup>4</sup> This approach led to the development of a novel general concept, namely, purpose-built materials,<sup>5</sup> which is dedicated to the design of novel metal oxide materials with the appropriate morphology, texture, and orientation in order to probe, tune, and optimize their physical properties.

In most cases, homogeneous nucleation of solid phases (metal oxides in particular) requires a higher activation energy barrier, and therefore, heteronucleation will be promoted and will be energetically more favorable (e.g., influence of seeding on crystal growth). Indeed, the interfacial energy between crystals and substrates is usually smaller than the interfacial energy between crystals and solutions. Consequently, (hetero)nucleation takes place at a lower saturation ratio onto a substrate than in homogeneous solution. Epitaxial crystal growth occurs from substrate-generated nuclei along the easy direction of crystallization, and if the concentration of precursors is high, a condensed phase of single-crystalline rods perpendicular to the substrate is obtained. Recently, such approach has been successfully applied to the design of large arrays of three-dimensional crystalline highly oriented hematite nanorod array,<sup>6</sup> whose unique structural design led to a two-dimensional quantum confinement<sup>7</sup> as well as an incident photon-to-electron conversion efficiency (IPCE) of 60% at 350 nm.<sup>8</sup>

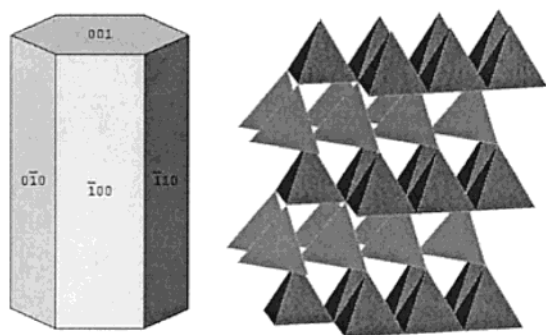
Zinc oxide represents an important basic material due to its low-cost, large-band gap, and luminescent properties.<sup>9</sup> It is commonly used as white pigment and extensively theoretically and industrially studied as catalysts,<sup>10,11</sup> for instance, for the production of methanol. It is also widely investigated as gas

sensors<sup>12,13</sup> due to its increase in surface conductivity upon adsorption and as transparent conductive oxide<sup>14</sup> (TCO), varistors,<sup>15</sup> piezoelectric<sup>16</sup> devices, and electroacoustic transducers.<sup>17</sup> Its optoelectronic properties have also been under scrutiny for photoanodes,<sup>18</sup> short-wavelength lasing,<sup>19,20</sup> and cathodoluminescence<sup>21</sup> due to its broad emission band in the yellow-green region as well as for the general nonlinear optical properties of II-VI semiconductors.<sup>22</sup> Recently, photovoltaic devices based on bare<sup>23</sup> and dye-sensitized thin films<sup>24–26</sup> have shown the great potential of ZnO for such applications. It has also been newly proposed<sup>27</sup> as an alternative substrate for the epitaxial growth of GaN and InGaN due to its isomorphism and excellent lattice match. Such process should significantly lower the creation of high dislocation densities in these compounds, which shortens substantially the operation lifetime of high-power transistors and laser diodes. Accordingly, designing novel ZnO material and, in particular, well-defined anisotropic and highly oriented 3D large arrays is of great importance for basic fundamental research as well as of relevance for various fields of industrial and high-technology applications.

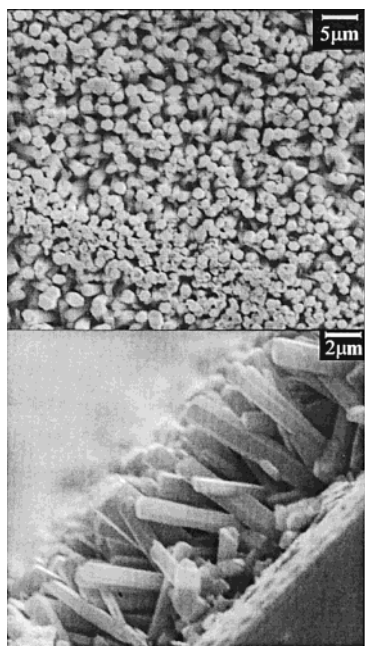
The thermodynamically stable crystallographic phase of this polar nontransition metal oxide is wurtzite and occurs in nature as the mineral Zincite (although scarcely as natural single crystal). Its ionic and polar structure can be described as a hexagonal close packing (HCP) of oxygen and zinc atoms in point group 3m and space group  $P6_3mc$  with zinc atoms in tetrahedral sites. The occupancy of four of the eight tetrahedral sites of HCP arrays controls the structure. The hexagonal unit cell contains two formula units, and the crystal habit exhibits a basal polar plane (00 $\bar{1}$ ) and two types of low-index faces, a nonpolar ( $\bar{1}00$ ) face (and  $C_{6v}$  symmetric ones) and a tetrahedron corner-exposed polar (001) face (Figure 1). The “low-symmetry” nonpolar faces with 3-fold coordinated atoms are the most stable ones. Additionally, there is no center of inversion in the wurtzite structure, and therefore, an inherent asymmetry along the *c*-axis is present allowing the growth of anisotropic crystallites.

Due to the very low tendency of divalent metal ions to precipitate in aqueous solution by hydrolysis–condensation in neutral or acidic medium<sup>28</sup> (compared to metal ions with higher oxidation state such as Fe<sup>3+</sup> or Cr<sup>3+</sup>), the synthesis was conducted by aqueous thermal decomposition of Zn<sup>2+</sup> amino complex with reagent-grade chemicals. A regular stopped flask containing, for instance, a polycrystalline F–SnO<sub>2</sub> glass sub-

\* Corresponding author. Email: lionel@fki.uu.se. Fax: +4618508542.



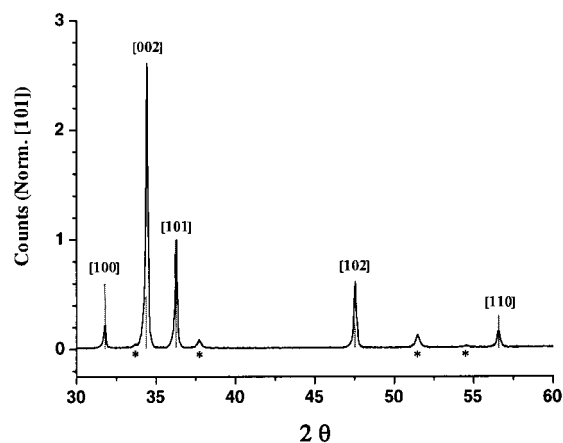
**Figure 1.** Crystal habit and crystal structure of ZnO (zincite).



**Figure 2.** FEG-SEM micrographs of ZnO microrod array grown onto transparent conducting tin oxide glass substrate.

strate (e.g., Hartford Glass Inc.), a Si or SiO<sub>2</sub> wafer, a bare piece of glass or a conducting plastic (e.g., ITO on polyester) substrate, and an equimolar (0.1 M) aqueous solution (MilliQ, 18.2 MΩ) of zinc nitrate, Zn(NO<sub>3</sub>)<sub>2</sub>·4H<sub>2</sub>O, and methenamine, C<sub>6</sub>H<sub>12</sub>N<sub>4</sub>, is placed in a regular laboratory oven and heated at 95 °C for 1–10 h, depending on the required microrod length. Subsequently, the thin films are thoroughly washed with water to remove any residual salt or amino complex and allowed to dry in air at room temperature.

As expected, well-aligned single-crystalline hexagonal rods of typically 1 μm in diameter showing well-defined crystallographic faces are grown along the [001] direction in a perpendicular fashion onto the substrates and arranged in very large uniform arrays (Figure 2). XPS analysis performed at synchrotron facilities do not reveal any surface contamination of the samples. According to electron diffraction and XRD, zincite ZnO (wurtzite structure) is the only crystallographic phase detectable. Since the material is readily crystalline, no additional heat treatment is necessary, which allows, for instance, the use of flexible and/or temperature-sensitive substrates. However, the mechanical properties of the microrod array are improved after heat treatment. Figure 3 shows the XRD pattern of the highly oriented microrod array of ZnO, which illustrates the texture effect of the anisotropic morphology and orientation on the relative intensity of the diffraction peak (normalized to [101] line which usually corresponds to the



**Figure 3.** XRD pattern (Cu Kα) of the ZnO microrod array on F-SnO<sub>2</sub> glass substrate (\*). The intensity was normalized to the [101] peak. Dashed lines represent the usual relative intensity of ZnO.

maximum intensity of ZnO zincite). As expected, a substantially higher intensity is obtained for the [002] diffraction peak.

Several tens of square centimeter arrays (and potentially much larger with larger substrate and container) are easily produced. While the width of the microrods is fixed to about 1 μm, their length, which essentially represents the thickness of a homogeneous monolayer of the thin film, may be experimentally tailored, over 2 orders of magnitude, to any required dimension of up to 10 μm by adjusting the synthesis time (i.e., a growth rate of approximately 1 μm per hour at 95 °C).

Various types of substrates have been investigated, and it appears that the type and crystallinity of the substrates tested had almost no influence on the crystal growth and orientation of the ZnO microrod array. However, it has been reported earlier that zinc oxide grown from sputtering techniques was greatly influenced by the surface crystallinity of the substrates.<sup>29</sup>

Growing large arrays of nano-/microcrystallites with well-controlled orientation and morphology allows carrying out large-scale measurements on well-known and well-defined surfaces. Therefore, by performing UHV single-crystal experiments as well as quantum calculation and molecular dynamics simulation studies on similar surfaces, one may reach better fundamental understanding on the relation between the electronic and bulk/interface structure (e.g., anisotropy and surface polarity) of the material and its particular efficiency or catalytic activity. Consequently, a direct feedback between modeling and experimental data should contribute to the improvement and optimization of ZnO-based devices as well as to obtaining better comprehensive fundamental knowledge of the investigated physical/chemical properties.

In addition, the particular architecture of this novel material allows in-depth study of the electron transport properties, fluorescence yields, and luminescence properties of ZnO as a function of the aspect ratio (variation in length) of the microrods for instance by laser spectroscopy. The photoelectrochemical properties in the UV and visible range (via dye-sensitization) and the electronic structure of such novel highly oriented anisotropic material are currently under investigation in our department and at synchrotron facilities to probe, for instance, the symmetry and the contributions of the oxygen 2p<sub>x,y,z</sub> orbitals on the conduction band of ZnO by polarization-dependent soft X-ray spectroscopy.<sup>30</sup>

**Acknowledgment.** This work was supported by the Swedish Material Research Consortium on Clusters and Ultrafine particles.

## References and Notes

- (1) Martin, C. R. *Chem. Mater.* **1996**, 8 (8), 1739–1746.
- (2) Xia, Y.; Rogers, J. A.; Paul, K. E.; Whitesides, G. M. *Chem. Rev.* **1999**, 99 (7), 1823–1848.
- (3) Liu, R.; Vertegel, A.; Bohannon, E. W.; Sorenson, T. A.; Switzer, J. A. *Chem. Mater.* **2001**, 13 (2), 508–512.
- (4) Vayssieres, L. Ph.D. Dissertation, Université Pierre & Marie Curie, Paris, France, 1995.
- (5) Vayssieres, L.; Hagfeldt, A.; Lindquist, S.-E. *Pure Appl. Chem.* **2000**, 72 (1-2), 47–52.
- (6) Vayssieres, L.; Beermann, N.; Lindquist, S.-E.; Hagfeldt, A. *Chem. Mater.* **2001**, 13 (2), 233–235.
- (7) Guo, J.-H.; Vayssieres, L.; S  the, C.; Butorin, S.; Nordgren, J. Manuscript to be published.
- (8) Beermann, N.; Vayssieres, L.; Lindquist, S.-E.; Hagfeldt, A. *J. Electrochem. Soc.* **2000**, 147 (7), 2456–2461.
- (9) Zhong, J.; Kitai, A. H.; Mascher, P.; Puff, W. *J. Electrochem Soc.* **1993**, 140 (12), 3644–3649.
- (10) King, D. S.; Nix, R. M. *J. Catal.* **1996**, 160, 76–83.
- (11) Yoshimoto, M.; Takagi, S.; Umemura, Y.; Hada, M.; Nakatsuji, H. *J. Catal.* **1998**, 173, 53–63.
- (12) Lehman, H. W.; Widmer, R. *J. Appl. Phys.* **1973**, 44, 3868.
- (13) Trivikrama Rao, G. S.; Tarakarama Rao, D. *Sens. Actuators, B* **1999**, 55, 166–169.
- (14) Minami, T. *MRS Bull.* **2000**, 25 (8), 38–44.
- (15) Sousa, V. C.; Segadaes, A. M.; Morelli, M. R.; Kiminami, R. H. G. A. *Int. J. Inorg. Chem.* **1999**, 1, 235–241.
- (16) Agarwal, G.; Speyer, R. F. *J. Electrochem. Soc.* **1998**, 145 (8), 2920–2925.
- (17) Quaranta, F.; Valentini, A.; Rizzi, F. R.; Casamassima, G. *J. Appl. Phys.* **1993**, 74 (1), 244–248.
- (18) Schoenmakers, G. H.; Vanmaekelbergh, D.; Kelly, J. J. *J. Phys. Chem.* **1996**, 100 (8), 3215–3220.
- (19) Bagnall, D. M.; Chen, Y. F.; Zhu, Z.; Yao, T.; Koyama, S.; Shen, M. Y.; Goto, T. *Appl. Phys. Lett.* **1997**, 70 (17), 2230–2232.
- (20) Reynolds, D. C.; Look, D. C.; Jogai, B. *Solid State Commun.* **1996**, 99 (12), 873–875.
- (21) Bylander, E. G. *J. Appl. Phys.* **1978**, 49 (3), 1188.
- (22) Klingshirn, C.; Kalt, H.; Renner, R.; Fodorra, F. *J. Cryst. Growth* **1985**, 72, 304–312.
- (23) Keis, K.; Vayssieres, L.; Rensmo, H.; Lindquist, S.-E.; Hagfeldt, A. *J. Electrochem. Soc.* **2001**, 148 (2), A149–155.
- (24) Tennakone, K.; Kumara, G. R. R. A.; Kottegoda, I. R. M.; Perera, V. P. S. *Chem. Commun.* **1999**, 15–16.
- (25) Rensmo, H.; Keis, K.; Lindstr  m, H.; S  dergren, S.; Solbrand, A.; Hagfeldt, A.; Lindquist, S.-E.; Wang, L.; Muhammed, M. *J. Phys. Chem.* **1997**, 101 (14), 2598–2601.
- (26) Keis, K.; Vayssieres, L.; Lindquist, S.-E.; Hagfeldt, A. *Nanostruct. Mater.* **1999**, 12 (1–4), 487–490.
- (27) Nause, J. E. F. *III-Vs Rev.* **1999**, 12 (4), 28–31.
- (28) Baes, C. F.; Mesmer, R. E. *The Hydrolysis of Cations*; Wiley: New York, 1976.
- (29) Yoshino, Y.; Inoue, K.; Takeuchi, M.; Makino, T.; Katayama, Y.; Hata, T. *Vacuum* **2000**, 59, 403–410.
- (30) Guo, J.-H.; Vayssieres, L.; Persson, C.; Ahuja, R.; Nordgren, J. Manuscript to be published.