Morphology Control of Zinc Oxide Particles at Low Temperature

Yoshitake Masuda, Kazumi Kato
National Institute of Advanced Industrial Science and Technology (AIST),
2266-98 Anagahora, Shimoshidami, Moriyama-ku, Nagoya 463-8560, Japan
masuda-y@aist.go.jp
http://staff.aist.go.jp/masuda-y/index.html

We investigated the crystal growth of ZnO to control morphology of ZnO particles and particulate films. Crystalline ZnO was nucleated in an aqueous solution containing zinc nitrate hexahydrate and ethylenediamine at 60 °C and was grown to form multi-needle particles having ultrafine surface relief structure. The ZnO particles thus have a high specific surface area due to the many needles and surface relief structure. The ZnO particles were then deposited on a substrate to form particulate film and thin sheets were further grown to connect ZnO particles to each other and with a substrate. Thin sheets grown in a second step improved the mechanical strength of the particulate films and contributed to the increase of specific surface area. The ZnO particulate film having a high specific surface area, high mechanical strength and high electrical conductivity is a candidate base material of sensors and solar cells. Control of crystal growth and morphology of ZnO in an aqueous solution would contribute to the development of future inorganic devices and crystallography of oxide materials in solutions.

Morphology control of ZnO particles

Zinc nitrate hexahydrate (15 mM) was dissolved in distilled water at 60 °C and ethylenediamine (15 mM) was added to the solution to induce the formation of ZnO. Glass substrate was immersed in the middle of the solution at an angle and the solution was kept at 60 °C using a water bath for 80 min with no stirring. The solution became clouded shortly after the addition of ethylenediamine. Ethylenediamine plays an essential role in the formation of crystalline ZnO. ZnO was homogeneously nucleated and grown to form a large amount of particles to make the solution clouded. ZnO particles were gradually deposited and further grown on a substrate. Homogeneously nucleated particles precipitated gradually and the solution became light white after 80 min. The supersaturation degree of the solution was high at the initial stage of the reaction for the first 1 h and decreased as the color of the solution changed.

After having been immersed in the solution for 80 min, the substrate covered with ZnO particles was evaluated by SEM and XRD. ZnO particles were shown to be multi-needle shape in which many needles were grown from the center of the particles (Fig. 1). The particles have more needles compared with the particles previously reported which were constructed from two large needles and several small needles[1]. The size of particles was in the range from 1 – 5 μm which is larger than the particles prepared previously[1]. Needles were constructed from an assembly of narrow acicular crystals and thus the side surfaces of needles were covered with arrays of pleats. The tips of the needles were rounded V-shape with many asperities. Edged hexagonal shapes were observed at the tips of needles, thus clearly showing high crystallinity and the direction of the c-axis. The c-axis would be the long direction of multi-needles and narrow acicular crystals. Elongation of the c-axis observed by SEM is

consistent with high diffraction intensity of 0002. The 0002 diffraction intensity of multi-needle ZnO particles was much stronger than 10-10 or 10-11 peaks though 0002 diffraction is weaker than 10-10 or 10-11 diffractions in randomly orientated ZnO particles (JCPDS No. 36-1451). High diffraction intensity from (0002) planes which are perpendicular to the c-axis would be caused from the crystalline ZnO particles which grew to elongate the c-axis. The particles have more stacks of c-planes compared to that of (10-10) planes which are parallel to the c-axis or (10-11) planes and hence the intensity from (0002) planes was stronger than that from (10-10) or (10-11) planes.

ZnO grows to a hexagonal cylinder shape at low supersaturation degree because of its hexagonal crystal structure, however, ZnO grows to a multi-needle shape at high supersaturation degree which induces fast crystal growth. ZnO was thus grown to a multi-needle shape in our solution in spite of its hexagonal crystal structure. The growth of ZnO was halted by a rapid decrease of supersaturation degree and removal of particles from the solution to obtain ZnO multi-needle particles having an ultrafine surface relief structure. The morphology of the ZnO particles was controlled by the fast crystal growth due to high supersaturation degree and by the supression of crystal growth due to the rapid decrease of supersaturation degree and removal of particles from the solution.

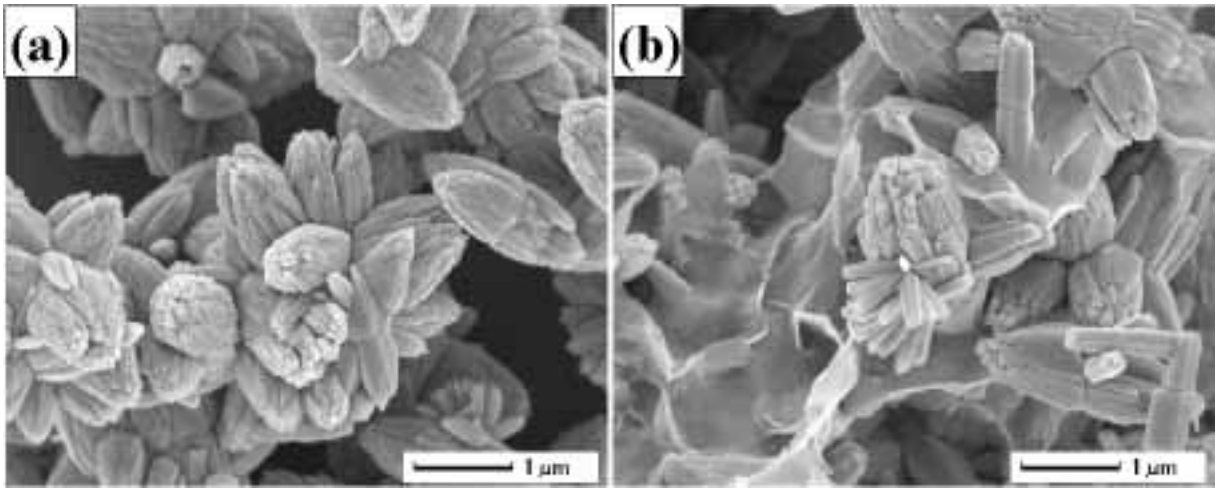

Fig. 1. SEM micrographs of (a) multi-needle ZnO particles having ultrafine surface relief structure and (b) ZnO particulate films constructed from ZnO particles and thin sheets.

(1)Masuda, Y.; Kinoshita, N.; Sato, F.; Koumoto, K. *Crystal Growth & Design* **2006**, *6*, 75-78.

Biographical Sketch

Name: Yoshitake Masuda
Born: Dec. 07, 1971
http://staff.aist.go.jp/masuda-y/index.html