

Design of Nanostructured ZnO Films by Electrochemical Deposition

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Zinc oxide (ZnO) is a II–VI group semiconductor material with a hexagonal Wurtzite crystal structure, a wide and direct bandgap of 3.37 eV (at 300 K), a large free-exciton binding energy (60 meV), a strong cohesive energy of 1.89 eV, a high optical gain (300 cm^{-1}), high mechanical and thermal stabilities, and radiation hardness. ZnO possesses a wurtzite structure similar to GaN, which is widely used in high-performance optoelectronic devices. This oxide is a promising candidate material for advanced applications due to the above-mentioned characteristics and unique combination of optical, electrical, magnetic, piezoelectric, ferromagnetism and surface reactivity properties.

We have developed various techniques for the electrochemical design of ZnO nanostructured films. The structures are controlled by playing on many deposition parameters such as the deposition temperature, deposition time and applied potential/current, precursor concentration and additives. The deposition principle consists in mixing a zinc salt with a hydroxide precursor and to generate hydroxide near the electrode by an electrochemical reduction reaction. Molecular oxygen is a classical and clean precursor since its electrochemical reduction only produces OH^- without any other by-product. Using a bath depleted in Zn(II) gives rise to the growth of ZnO NWs arrays which density, length and aspect ratio can be easily controlled.[1] Due to the low precursor concentration, the lateral growth of the wires is rapidly stopped and the growth only occurs along the c-axis. The wires are grown at rather high temperature and photoluminescence measurements have shown that the structural quality of the wires markedly increases with the deposition temperature.[2,3] By using templated substrates, organized arrays such as urchin-like hollow structures in which the spines of the urchins are made of ZnO nanowires, can be prepared.[4]

By increasing the Zn(II) concentration, dense and smooth films are grown at high temperature of the aqueous bath. On the other hand, when the temperature is close to room temperature, the nucleation on the electrode surface is difficult, first some hydroxide is formed which is slowly dehydrated with the deposition time. The film is made of small nanocrystallites of about 20 nm in diameter.[5]

Other original structures have been prepared by occlusion electrolysis.[6] In this case, ZnO particles with 400 nm mean size are added in the ZnO electrodeposition bath and by controlling the deposition solution flux toward the electrode, it is possible to get a film made of the particles, cemented by electrodeposited ZnO. The films presented large pores and were highly light scattering.

The film structure can also be controlled by using an organic additive (dye, polymer, amino acid...) in the deposition bath that is integrated in the electrodeposited

film and acts as a structure directing agent. For instance, textured nanoporous films with pore size of about 10 nm have been synthesized by using eosin Y as a structure directing agent.[7]

The electrodeposited structures can be combined and many combinations are possible. For instance, one can first grow an array of ZnO nanowires and, in a second step, grow nanocrystalline ZnO. The presence of ZnO nanowire backbones favor the growth of an epitaxial oxide and well-crystallization.[8] The coating is porous and the pores are oriented perpendicular to the wire surface (see figure). The most exposed ZnO planes are the (001), whereas they were (100)-oriented in the case of the nanoporous films prepared with eosin Y. Similar hierarchical structures have also been synthesized using the large particle film prepared by occlusion electrolysis. Some applications of the electrodeposited structures will also be presented such as to dye-sensitized solar cells, LED and sensors.

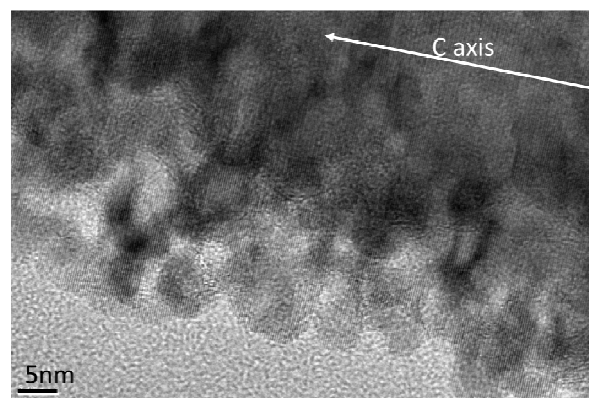


Figure: ZnO nanowire backbone covered by a conformal epitaxial shell of nanocrystalline porous ZnO.

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