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Growth Model for Nanoplates and Nanoboxes of Zinc Oxide from a Catalyst-Free Combust-Oxidized Process

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A novel growth model is proposed for ZnO nanoplates and nanoboxes that are produced via a catalyst-free combust-oxidized (CFCO) process. In the CFCO process, molten zinc is vaporized and instantaneously oxidized in normal atmosphere to produce zinc oxide crystals that are transported into a 100–180 m cooling duct. FESEM analyses show clear images of quasi-rectangular nanoplates and nanoboxes. The plates and boxes can be differentiated by the width-to-height ratio (W/H ratio) whereby a W/H ratio of (0.5–1.5) refers to nanoboxes while other ratios classify the nanoplates. These rectangular nanostructures generally have $\langle 10\bar{1}0\rangle$ plane growth direction. We propose growth starts from two kinds of nucleation planes parallel to the six-sided $\{10\bar{1}0\}$ facets of nanorods that provide the nucleation sites for the nucleation planes.

Keywords ZnO, nanostructure, varistor, CFCO, nanoplate, nanobox

INTRODUCTION

Commercially produced zinc oxide is mainly manufactured via a catalyst-free combust-oxidized (CFCO) process or commonly known as French process. ZnO is used in diversified applications that include electronics, rubber, paint, ceramics, pharmaceuticals and cosmetics. The CFCO furnace (Figure 1) consists of a graphite crucible inserted inside a cylindrical furnace made of firebrick. The design is a muffle type whereby hot flame from a burner heats up the crucible by convection, and heat is transferred to the zinc ingots (inside the crucible) via conduction through the graphite lining. Zinc melts at 420°C with heat of fusion 6.67 kJ/mol, boils at 907°C with heat of vaporization 114.2 kJ/mol and possesses a critical temperature of 3107°C.[1] The crucible is covered with a graphite lid to pressurize the zinc vapor trapped inside the crucible where zinc vapor temperature rises as its pressure increases. Once the orifice lid is removed, the pressure difference causes the zinc vapor to purge out and it is instantaneously oxidized in ambient air. The zinc vapor has a nozzle temperature of 1100–1400°C and a nozzle speed of about 8–12 m/s (calculated). Some manufacturers build an enclosure around the combustion chamber in order to control the oxygen-to-zinc ratio and to stabilize the temperature.

Oxidation and crystal growth take place in the combustion area. A unique feature of the temperature profile (Figure 1c) is the sudden 1100°C–800°C temperature drop between the crucible orifice and top part of the conical suction hood (Figure 1a). Not only the ZnO growth time is very short (in seconds), a large variety of one-dimensional nanostructures of zinc oxide can be formed which includes nanorods, nanoplates, nanoboxes, irregularly-shaped particles (ISPs), polyhedral drums and nanomallets, as presented in Figure 2. The *superfast growth time* makes the CFCO process the most productive way to mass-produce ZnO powder at a rate of 70–100 kg/h, depending on the furnace design and nozzle temperature. From the combustion area, the newly formed ZnO is transported by suction into a 100–180 m long cooling duct with an average mass flowrate of 1.1–1.5 kg/min and with a temperature profile posted in Figure 1c.

Due to highly nonuniform crystallization conditions in the combustion chamber, the diverse ZnO nanostructures can coexist (and codiffuse) even in a minute region of 1 μm^3, giving rise to the state of *nanoscopic inhomogeneity* (Figure 2). To date, little work has been undertaken to

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