

# Nanostructure of ZnO Fabricated via French Process and its Correlation to Electrical Properties of Semiconducting Varistors

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The rich nanostructural diversity of commercial zinc oxide, fabricated via French process, is investigated. FESEM images of ZnO nanostructures reveal nanorods, nanoplates, nanoboxes, nanomallets, microclusters, polyhedral drums and irregularly-shaped particles (ISPs). Due to nanoscopic inhomogeneity in crystallisation conditions, many types of ZnO nanostructures coexist (and codiffuse) even in a minute region of  $1\ \mu\text{m}^3$ . The nanostructures generally grow in either the [0001] or the  $[10\bar{1}0]$  plane directions. EDS analysis reveals that hexagonal-like nanorods/drums possess higher oxygen-to-zinc atomic ratios than that of the rectangular-like nanoplates/boxes. A correlation between ZnO nanostructure and semiconducting varistors shows that nanorod-rich specimens exhibit superior nonlinearity but poorer energy handling.

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**Keywords** ZnO, nanostructure, varistor, French process

## INTRODUCTION

In the recent decade, a large variety of zinc oxide nanostructures such as rods, wires, needles, belts, discs, tetrapods, mallets, tubes and cages, have been fabricated via several growth techniques that include plasma molecular beam epitaxy, vapor phase transport, metal organic vapor-phase

epitaxy and vapor-liquid-solid (VLS) process.<sup>[1–5]</sup> A huge majority of commercial zinc oxide is manufactured using the French process, a four-decade old technology, which is the cheapest and highly productive method to mass-produce ZnO that is used in diversified applications such as electronics, rubber, paint, ceramics, pharmaceuticals and cosmetics. In the French process, molten zinc is vaporised at 1000–1400 °C and instantly air-oxidised into ZnO powder, which is transported into a 100–200 m cooling duct. Due to highly nonuniform crystallization conditions, particularly oxygen partial pressure, many types of one-dimensional nanostructures can coexist (and codiffuse) with one another. Zinc oxide nanorods, nanoplates, nanoboxes and irregularly shaped particles (ISPs) are typical nanostructures found in French-process ZnO. To date, little work has been undertaken to investigate the growth of these fascinating nanostructures and the impact on their applications.

## THEORY

ZnO is a II-VI compound semiconductor possessing a hexagonal wurtzite structure (space group  $P6_3mc$ ) with lattice parameters  $a = 0.32495\ \text{nm}$  and  $c = 0.52069\ \text{nm}$ . It has a wide direct bandgap of 3.37 eV and a large exciton binding energy of 60 meV. ZnO readily grows to form one-dimensional nanostructures with three fast growth directions,  $\langle 01\bar{1}0 \rangle$ ,  $\langle 2\bar{1}\bar{1}0 \rangle$  and  $\pm[0001]$ , whereby the first two growth directions tend to produce nonpolar surfaces with lower energy than that of the  $\{0001\}$  polar facets.<sup>[3,6,7]</sup> ZnO varistors, with about 90% ZnO weight content, are semiconducting surge suppressors extensively used in power-related applications.<sup>[8–12]</sup> The nonlinear coefficient ( $\alpha$ ) is an important figure of merit whereby large  $\alpha$  values offer excellent response for electrical surge suppression. The nonlinear

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