Synthesis and Reactivity in Inorganic, Metal-Organic and Nano-Metal Chemistry, 36:59–64, 2006

ISSN: 0094-5714 print / 1532-2440 online
DOI: 10.1080/15533170500471730

Increase in Upturn Power Dissipation of Surge Suppressors Due to Highly Defective Nanostructure of Zinc Oxide

Shahrom Mahmud and Mat Johar Abdullah
University of Science, Malaysia, Penang, Malaysia

Ghanim A. Putrus
Northumbria University, Newcastle upon Tyne, U.K

Nanodefects are probable root causes for the observed high power dissipation of ZnO-based surge suppression devices (SSDs). In this work, nanodefects are introduced by overgrinding ZnO for 100 hours via wet milling. Using FESEM, ZnO nanostructures are found to contain fine cracks, chipped-off surfaces and nanofragments. For the defective ZnO, the zinc relative atomic % (EDS analysis) is observed to be much larger accompanied by higher oxygen vacancy concentration as revealed by PL green emission. Average particle size drops from 0.24 μm to 0.19 μm and specific surface area increases from 4.72 m^2/g to 5.67 m^2/g. Fabricated SSDs with defective ZnO exhibits higher power dissipation and bigger grain resistivity. A model is proposed to provide a correlation between nanodefects and power dissipation.

Keywords surge suppressor, varistor, nanodefects, power dissipation, ZnO

INTRODUCTION

Wet milling could be the most widely used commercial technique to mix and mill ZnO powder with metal oxides and frits in order to manufacture ZnO-based electrical surge suppression devices (SSDs) or commonly known as varistors. To date, little work is undertaken to investigate the impact of overmilling (or overgrinding) on the electrical characteristics of semiconducting ZnO SSDs. The mechanical impact of cascading grinding media on ZnO crystallites causes the breaking of particles into smaller micro and nanofragments. Microclusters and agglomerates are broken down into individual particles with chipped edges such that they nearly lose their hexagonal or rectangular crystallographic appearance (Figure 1). Wet milling beyond 50 hours can reduce the average particle size by about 20% accompanied by a 20% increase in specific surface area (SSA), which is desirable to obtain large ZnO grains (exceeding 100 μm) at sintering. Large grains are needed to manufacture varistors that are used for low-voltage models below 25 V_{rms} operating voltage. The trade-off of obtaining large grains via overmilling is the large increase of nanodefects (dislocations, interstitials and vacancies) when broken surfaces result from the impact. Donor and trap densities are greatly affected if the nanodefect concentration is large enough. Subsequently, other electrical characteristics such as nonlinearity, grain resistivity and power dissipation are also influenced.[1]

THEORY

About 90% of ZnO-based surge suppressors (varistors) are made up of zinc oxide material while the other ingredients are normally oxides of Bi, Sb, Co, Mn, Ti, Al, Ni, Cr or Si. For each ZnO unit cell, there are a maximum of 17 interstitial sites (16 Power dissipation and ZnO nanostructure tetrahedral and 1 octahedral) and they can be occupied by extrinsic interstitials (dopants) or intrinsic interstitials (zinc) provided that the atomic radius ratio is in the range of 0.225–0.732.[2] Since large ions such as bismuth (0.12 nm) cannot occupy the sites, they are segregated to the grain boundary where bismuth forms bismuth-rich phase that is crucial for the formation of the varistor action (band-bending capability). Bismuth also contributes in providing oxygen diffusion paths that facilitate the formation of grain boundary electrical states or Schottky potential barriers.[3–5]

A common phenomenon of hexagonal wurtzite ZnO is an appreciable level of natural-occurring intrinsic defects (excess zinc) that produces a non-stoichiometric compound $Zn_{1+d}O$.[6,7] These excess zinc act as donor interstitials that tend to occupy special interstitials sites with Miller indices (1/3, 2/3, 0.875) in the wurtzite lattice.[8] These special sites offer passage routes for zinc interstitials to easily migrate within the ZnO structure. In highly defective ZnO, the concentration of excess zinc is expected to be large enough to significantly

Received 20 July 2005; accepted 28 October 2005.
Address correspondence to Shahrom Mahmud, University of Science, Malaysia, 11800, Penang, Malaysia. E-mail: shahromx@yahoo.co.uk