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Zn-dust derived ultrafine grained ZnO non-linear ceramic resistors via in-situ thermal oxidation of cermet reactant mixture

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ABSTRACT

Ceramic–metal composite (cermet) varistor mixture was processed by mechanical blending of micron sized metallic Zn dust with rare earth oxides (La_2O_3, CeO_2) and other varistor forming minor additives (CoO, Cr_2O_3, Al_2O_3, MnO_2 and SiO_2). Toxic Bi_2O_3 and Sb_2O_3 additives were avoided. The cermet varistor mixture was uniaxially pressed into cylindrical pellets and sintered at various temperatures to obtain ZnO varistors. At 1250 °C, Zn dust derived cermet composition showed 99% theoretical density, average sintered grain size <2.5 μm, breakdown voltage $V_b = 477\ V\ mm^{-1}$ and non-linear coefficient $\alpha = 38$. A comparative study of varistor property was also performed with the commercial ZnO counterpart. The sintering analysis revealed early densification in cermet-derived ZnO varistors. In addition to varistor fabrication, temperature controlled production of ZnO nanostructures via direct thermal-oxidation of Zn dust was also investigated. Evolution of nanostructures was systematically analysed using TGA, XRD, SEM and TEM. From the microstructural analyses, the growth of well-defined ZnO nanowires with several micrometre length was confirmed. In this exploratory research, the results clearly suggest that Zn dust can be a potential source for technologically important nanostructures and for developing functional grade electronic devices such as miniaturized high energy field varistors.

1. Introduction

'Zinc dust' and 'zinc ash' are industrial by-products produced in bulk quantities via atomization during zinc alloy processing [1–3].The 'zinc dust' is a ductile grey coloured powder, having an average particle size of 5 to 15 μm. It is a strongly recommended and a largely consumed product in Zn-primer paints [2]. It is used in heavy-duty anti-corrosion protection coatings on textile, marine structures and steel sheets [4,5]. Other than the paint applications, 'Zn dust' has not been effectively utilized for developing any hi-tech industrial ceramics or for producing any functional nanostructures. But, its oxidic counterpart, ZnO, finds immense use in multifunctional semiconducting nano-devices [6–9], functional cosmetics [10], hydrophobic coatings [11], UV/IR shielding surfaces [12,13], and in sensing applications [14]. Thus, an increased demand exists in scientific and industrial field for developing size controlled ZnO powders and its nanostructures from its cheapest metallic alternative [7,9]. Till date, the use of 'Zn dust' as a source for ZnO nanostructures has not been explored in detail, even though 'Zn dust' is an easily available, low-cost raw material. The use of 'Zn dust' recovered from secondary sources like sulphide zinc concentrates for the production of nano ZnO put forwards a 'waste to wealth' concept, indirectly reducing the environmental impact and at the same time making economic benefits [2,3]. The techniques such as hydrothermal [7,15], pulsed laser and chemical vapour deposition [16–18], sol gel [19] and solochemical processing [20] methods are already attempted for synthesizing nano size ZnO. Varied morphologies viz. nanorods, nanobelts, nanowires, nanoblades and nanowhiskers were also resulted. But, the stringent and complex multi-step synthesis procedures and the poor reproducibility issues inhibit the current synthesis methods for the industrial scale up.

The direct oxidation of Zn dust is a non-catalytic approach for the oxidic nanomaterial production. It is advantageous in a way that one can grow unique size and shape controlled nano ZnO without much processing difficulties. In this process, the tailoring of nanostructure is possible by tuning the oxidation temperature and the heat treatment time [21,22]. Thus, the industrial scale up is also possible. Wang et al. reported the synthesis of nano ZnO by oxidizing metallic Zn particle prepared through an arc-discharge technique in air at different temperatures and time [21]. Growth of temperature dependent ZnO morphologies on high purity Zn foil was studied by Lu et al. [22]. Synthesis of ZnO nanowires by annealing metallic Zn nanowire made by heating ZnO and graphite mixture has also been attempted by Khan and Kordesch [23]. However, none of the studies explains the sequential evolution of ZnO nanostructures by direct thermal oxidation of Zn dust. Therefore, a systematic study is carried out in the present paper and the conversion of Zn dust

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to technologically feasible ZnO nanostructures was reported, with respect to temperatures.

Varistors are ceramic semiconductor device, widely used for over voltage protection in many areas of electronics and communication technology [8,24–29]. The use of zinc oxide for non-linear field control resistor (varistor) was reported by Matsuoka, four decades ago [30]. The varistor processing, still known in the name of its inventor Matsuoka, is being practised in industries. However, it has plenty of drawbacks. The main drawbacks of the current varistor processes are non-uniform distribution of minor additives, evaporation of minor dopants, and the formation of secondary spinel and pyrochlore phases [31,32]. All of the above mentioned problems resulted in an undesirable grain growth in ZnO (15–20 μm) ceramics. This limits the high energy handling capabilities of varistors [25,26]. Therefore, attempts are being made to fabricate ultra-fine grained ZnO varistors by controlling the grain size, through different preparation routes like sol–gel [26], precipitation [24], reflux [28] and combustion [29] methods. But, the direct use of Zn dust to fabricate ZnO varistor has not been either attempted or patented.

Thus, in the current study, we report the catalyst-free growth of ZnO nanostructures by direct thermal oxidation of metallic Zn dust. The structural features of nano ZnO and its transformation from highly crystalline rod to wire nanostructures with temperatures were systematically investigated and presented. Also, the effect of in-situ thermal oxidation of metallic Zn dust derived cermet composition for having fine-grained ZnO varistor ceramics was explored. To the best of our knowledge, such exploratory research on Zn dust was not attempted and the beneficial properties of economically cheaper 'cermet' source for varistor applications are not explored. The sintering of cermet compacts, evolution of varistor microstructures, I–V characteristics and dielectric properties of varistors derived from cermet mixture were studied in detail. A comparative study was also performed with the commercial ZnO derived counterpart.

2. Experimental details

2.1. Materials

Zinc dust (Binani Zinc Pvt Ltd. India, 99.9%) and zinc oxide (Sigma Aldrich 99.0%) were used as two different precursors of ZnO. Lanthanum nitrate (Alfa Acer, 99.99%), Cerium nitrate (Sigma Aldrich, 99%), Chromium nitrate (Sigma Aldrich, 99%), Aluminium nitrate (Merck, 95%), Silicon dioxide (Sigma Aldrich, 99.5%), Manganese acetate (Sigma Aldrich, 98%) and Cobalt nitrate (Sigma Aldrich, 99%) were used as varistor additives for cermet-varistor mixture.

2.2. Direct thermal oxidation of metallic Zn dust

The raw metallic Zn dust was taken in deionised water and ball milled for 60 h, using zirconia balls. The milled product was collected by centrifugal filtration and washed with ethanol solvent. It was dried overnight at 60 °C. The thermal oxidation was carried out in a muffle furnace in air atmosphere at temperatures ranging from 700–1000 °C. For oxidation, specific amount of Zn dust was taken in alumina ceramic boat and was loaded into the furnace. The sample was heated to the desired temperature, at a rate of 10 °C min^{-1} and was soaked for 2 h. After oxidation, the furnace was cooled to room temperature at a normal cooling rate. Finally, the oxidised samples at different temperatures were collected and analysed.

2.3. Fabrication of ZnO varistor from cermet mixture

Varistor composition equivalent to, 97.1 mol% ZnO (9.39 g) + 0.5 mol% La_2O_3 (0.19 g) + 0.5 mol% CeO_2 (0.10 g) + 0.5 mol% Cr_2O_3 (0.09 g) + 0.5 mol% CoO (0.15 g) + 0.5 mol% SiO_2 (0.03 g) + 0.2 mol% Al_2O_3 (0.02 g) + 0.2 mol% MnO_2 (0.03 g), was initially prepared. The precursors were charged into polypropylene milling jars (250 cm^3 vessel volume), mechanically milled by Zirconia balls (10 mm dia.) in ethanol medium using a motor driven ball mill (250 rpm) for a period of 24 h. It was then dried at overnight, at a temperature of 60 °C. The dried powder was then calcined at 600 °C for the decomposition of the volatile nitrates. The cermet powder was pressed into cylindrical discs of 10 mm diameter and 1 mm thickness at a pressure of 100 MPa. 1 ml of 0.5% PVA was used as the binder material. The cermet pellets were sintered at 1100, 1200, 1250 and 1300 °C in air for 2 h. Sintering was carried out at a heating rate of 3 °C min^{-1}. At 600 °C, a soaking of 20 min was given to the sample to ensure the removal of organic binder. At peak temperatures, a soaking time of 2 h was given to the sample to facilitate the complete oxidation and densification. Either side of the sintered varistor discs were lapped with SiC paper and polished with 3 μm diamond suspension to a mirror finish. The samples were etched at a temperature 1000 °C. For comparison, varistor discs were also processed from commercial ZnO powder (Aldrich chemicals, 99.0%). Cermet varistor powder processed from the metallic Zn dust was compared with varistor mixture made out of commercial ZnO under identical mixing–milling conditions. Both samples were characterized for the particle size, phase analysis, densification and microstructural features. For convenience, varistors processed from Zn dust are named as 'cermet route' and the latter as 'oxide route' systems.

3. Characterization

The ZnO nanostructures and varistor samples processed in the present study were systematically characterized using various techniques. The density of the sintered varistors processed via both cermet and oxide routes were measured by Archimedes technique, using the relation,

$$\rho_{experimental} = W_{air}/(W_{air} - W_{water}) \quad (1)$$

where, W_{air} and W_{water} are the weights of sample in air and water respectively. Crystalline phases of ZnO and Zn dust were characterized by an X-ray diffraction (XRD) Philips X'PertPro diffractometer in the 2θ angle range 20–80° using CuKα radiation (λ = 1.54178 Å). Particle size distribution was examined using Malvern zeta seizer (NANO ZS). Thermal decomposition and melting behaviour of Zn dust was analysed using thermo gravimetric analyser (TGA) (Shimadzu H TGA-50). The samples were heated from room temperature (35 °C) to 800 °C at the heating rate of 10 °C min^{-1} in oxygen atmosphere with a flow rate of 50 mL min^{-1}. The sintering behaviour of Zn and ZnO were studied by thermomechanical analyser (TMA) (TMA-60 H Shimadzu). Particle morphology and microstructural features of Zn dust at various stages of processing as well as the grain and grain boundary distribution of varistors were observed under Zeiss EVO 18 special edition scanning electron microscope (SEM) operated at 20 KV. Transmission electron microscope images of the nanostructures were recorded using a FEI Tecnai 30G2S — TWIN transmission electron microscope (TEM) operated at an accelerating voltage of 300 kV.

3.1. Electrical characterization and dielectric measurements

Sintered varistor discs, with thickness 1 mm and diameter 10 mm, were electroded with conducting silver paste coatings on both surfaces for electrical and dielectric measurements. The V–I analysis of the varistors was done using an electrometer/high resistance metre (Keithley 2410, India) having a built-in voltage up to 1000 V and 1 mA current limit. The current passing through the sample was monitored for every 10 V. The electric field corresponding to 1 mA cm^{-2} current density was taken as the breakdown field. The leakage current (J_L) was calculated as the current at $0{\cdot}80 \times E_{1\ mA}$ (where, $E_{1\ mA}$ is the electric field