MICROEMULSION MEDIATED SYNTHESIS OF ZINC-OXIDE NANOPARTICLES FOR VARISTOR STUDIES

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ABSTRACT

This paper describes a microemulsion-mediated synthesis of zinc oxide nanoparticles for varistor studies and possible applications. These ultrafine polycrystalline ZnO nanoparticles have size ranging from 5-40 nm ESD. The microstructure, high density and electrical conductivity of sintered disks of pure and doped ZnO nanoparticles resulting from clean interfaces of particles and scaled down size of grains are found to result in a higher critical electric field and a higher coefficient of non-linearity (α) in the logE *versus* logJ curve. Significant developments will rely on further understanding of structure-property relationships.
MATERIALS INDEX: Varistor, microemulsion, nanoparticles, nanostructure.

Introduction

Nanometer-sized solids have found numerous applications in science and technology (1). Zinc oxide powder is widely utilized for functional devices (sensor, varistor, etc.), pigments, electrography, medical materials, etc. Synthesis of ultrafine powders of high purity and controlled particle shape and size is the primary step in the production of varistors with reliable ceramic and electrical properties (2). Their individual characteristics depend on both their chemical composition and the processes by which they are synthesized. Various

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methods generally adopted for the preparation of zinc oxide particles are the sol-gel method (3), the evaporation of solutions and suspensions (4), evaporative decomposition of solution (EDS) (5), conventional ceramic fabrication (6,7) and wet chemical synthesis (8,9). The synthesis of ZnO powder or film by gas-phase reaction between bis(acetyl acetonato)zinc(II) and water is also reported (10). Metal alkoxides have also been used for the preparation of metal oxides from transition metal complexes in liquid phase (11). The zinc oxide varistors fabricated from relatively larger zinc oxide particles are inhomogeneous, irreproducible, require longer heat treatment times, have large grain size with considerable porosity. Porosity and non-uniformity limits the energy absorption by increasing oxidation or corrosion and decreases strength and thermal conductivity. Also, the current density fluctuates from point to point, channeling through the regions of least resistance producing high temperature regions or hot spots. High local currents develop and consequently, most disks fail by puncture at this weak spot causing irreversible degradation. This indicates the importance of varistor fabrication in a manner that assures homogeneity. This can be acheived by using a microemulsion mediated process for the synthesis of precursors for ZnO varistors. In this process the aqueous core of the water-in-oil microemulsions are used as constrained microreactors for the precipitation of precursor carbonates of ZnO nanoparticles.

Microemulsions consist of an oil phase, a water phase, a surfactant (and sometimes a cosurfactant) which possess specific physico-chemical properties such as transparency, isotropy, low viscosity and thermodynamic stability (12). This is the consequence of their microstructure which consists of dynamically unstable (however, long-lived) microvesicles, the wall of which are made by an alternation of surfactant and cosurfactant molecules surrounded by an external phase and encapsulating an internal phase. Microemulsions along with liquid crystals now form an important new subject of soft solids. In water-in-oil microemulsions, the aqueous phase (10-25 nm) consisting of the soluble metal salt is the internal phase, dispersed in the continuous external phase of hydrocarbon. Two identical microemulsions are prepared, one containing the zinc salt and the other containing the precipitating agent dissolved in water as the aqueous phase. These microdroplets continuously collide, coalesce and break again. During this process, inter-droplet exchange and nuclei aggregation takes place and, consequently, the precursor precipitate is formed in the aqueous core of microemulsion (13).

Nanoparticles have a variety of properties that are different and, often considerably improved in comparison to those of relatively larger particles. The predominant feature of nanophase materials is their compositional homogeneity and clean surfaces of high specific surface area. Their sintered disks form grains which have narrow grain size distribution, pure grain boundaries and inherent stability against grain growth (14). They are thus analogous to a variety of closed cell foam structures, which are stable despite the large surface energy stored in them. Preparation of nanoparticles by this process has been extensively carried out in our laboratory in the synthesis of silver halides (15), oxalate precursors for Y-Ba-Cu-O (16,17) and Bi-Pb-Sr-Ca-Cu-O (18) superconductors and precursors for barium ferrite magnetic particles of high coercivity (19).

It is reported that in ZnO varistors, granular interfaces have a crucial influence on breakdown voltage, leakage current and varistor degradation. Also, to increase the clamping voltage for a device of a given thickness, the size of the grains in the sintered disks needs to be decreased. Using the microemulsion-mediated process for ZnO synthesis provides an efficient way to decrease the grain size. Hence, adopting this process and correlating the electrical properties and microstructure can be helpful in predicting ways of improving the

varistor properties. The essential aspect is the Schottky barrier at the intergranular region arising from the migration of atomic defects, causing a charge depletion region.

Experimental

The microemulsion system used for the present study consisted of cetyl trimethyl ammonium bromide (CTAB, 99%; Fisher Scientific) as surfactant; 1-butanol (99.8%; Fisher Scientific) as co-surfactant; n-octane (reagent grade) as continuous oil phase and an aqueous solution as the dispersed phase (Table 1). For the preparation of particles, a microemulsion containing 0.1 M zinc nitrate (99.9% Aldrich) solution as the aqueous phase was mixed with another microemulsion containing the precipitating agent, ammonium carbonate as the aqueous phase. Continuous collision of these microdroplets leads to their coalescence and subsequent formation of zinc carbonate precipitate in the droplet. The surfactant monolayer inhibits the growth and coagulation of the carbonate particles. A detailed schematic representation of this process has been illustrated earlier (16,18). The zinc carbonate precipitate was separated by centrifuging. It was washed with a 1:1 mixture of methanol and chloroform to remove any oil or surfactant from the particles. The precipitate was dried at 100°C to yield zinc carbonate precursor particles.

To ascertain the efficacy of this method we made a parallel study of the properties of ZnO particles prepared by bulk precipitation method and those from conventional powder. The bulk precipitation was carried out by mixing together aqueous solutions of $Zn(NO_3)_2$ and $(NH_4)_2CO_3$, the molarity being the same as used for microemulsion synthesis. For the conventional powder, $ZnCO_3$ (99.8%; Fischer Scientific) was calcined at 250°C to obtain ZnO. For the varistor fabrication, dopants were added chemically by precipitation onto the ZnO particles to obtain an overall base composition of 96.5 mol% ZnO; 0.5 mol% Bi_2O_3; 1.0 mol% Sb_2O_3; 0.5 mol% MnO; 1.0 mol% CoO and 0.5 mol% Cr_2O_3.

TABLE-1

Details of the Composition of Microemulsions

	Microemulsion-I	Microemulsion-II	Weight %
Aqueous phase	0.1M $Zn(NO_3)_2$	0.1M $(NH_4)_2CO_3$	36%
Surfactant	CTAB	CTAB	10%
Cosurfactant	1-Butanol	1-Butanol	10%
Oil phase	n-Octane	n-Octane	44%

The thermogravimetric analysis and differential scanning calorimetry (DuPont 900) revealed the optimum temperature of calcination to be a little above the endothermic peak and weight loss dip (carbonate to oxide), 220°C. Surface area measurements were obtained by nitrogen gas adsorption (BET) on a Quantasorb Surface Area Analyser-Model QS-17. The powder sample was outgassed in nitrogen for 24h at 200°C prior to analysis. Powder

X-ray diffraction was carried out on a Philips APD 3720 X-Ray powder diffractometer using Cu-Kα radiation. ZnO pellets of 1 cm diameter were prepared using a uniaxial pressure of 70 MPa. (The pressure was deliberately kept low so as to indicate the relative efficacy of sinterability of powders from the three methods). These pellets were sintered at 1200°C for 2 h. Density of the sintered pellets was measured at 25°C by the Archimedes method using isooctane. Microstructural characterization of the sintered pellets was done by taking their scanning electron micrographs on a JEOL-6400 microscope. Finally the voltage-current characteristics were measured by coating the sintered discs with conductive silver paint on both surfaces to provide an ohmic contact using a Keithley 610C electrometer and a Bio-rad laboratories 500 Model d.c. power supply variable upto 500 V. The ohmic nature of the contact was established by finding a linear scaling of resistance with thickness of the sintered pellets, keeping all the other relevant parameters constant.

Results and Discussion

The governing equation for varistor performance is $I = CV^{\alpha}$, where C is a material parameter and α is a nonlinear exponent whose value is especially important near the critical field when the logE versus logJ curve flattens. Higher value of α indicates a narrow clamping or critical voltage band. The microstructure can be considered as a vehicle through which physical, chemical and electrical properties of the material are manifested. Microstructural characterization of the sintered ZnO disks prepared by three different methods, namely: bulk precipitation, conventional powder, and microemulsion synthesis were carried out. The material parameters which showed improvement in ZnO nanoparticulate doped sintered disks are a high degree of uniform density, combined with low porosity and uniform equiaxed grains. Another good result is the critical electric field value, E_c = 4.5 kV/cm (compared with E_c = 2.9 kV/cm for the conventional material). These manifest themselves in a very high value of α = 83 (compared with the conventional material having α = 29), Fig.1.
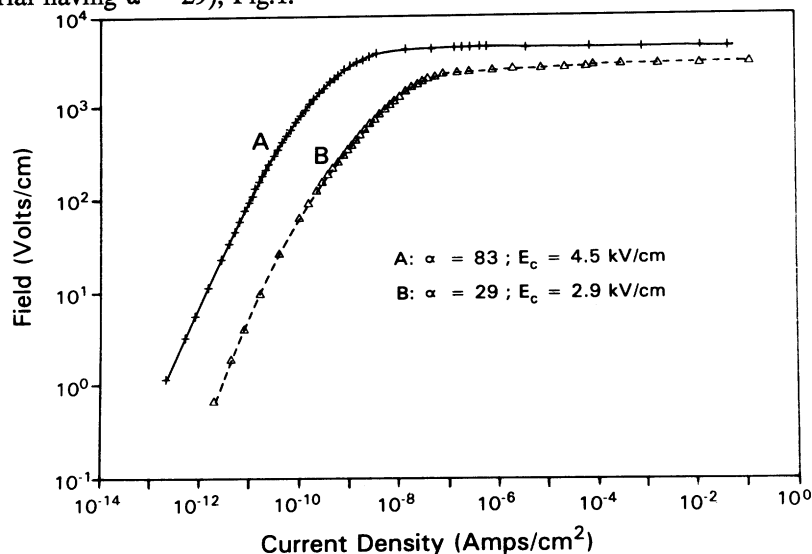

FIG.1

Results of the Voltage - Current measurements for the varistor composition indicated in text from ZnO particles prepared (A) in Microemulsion (B) Conventional powder.

So, we have begun this section by pointing to the reader straight away the final crux of the whole study which made further investigation essential and interesting.

For the evolution of such good parameters one needs to see the characteristics of the pure ZnO powder obtained by the three methods, development of their microstructure, and their electrical properties. Their X-ray diffraction pattern shows the characteristic pattern for ZnO. No other impurities were detected. X-Ray diffractograms of ZnO microemulsion-derived nanoparticles shows the broadest peak width which indicate that they have smallest mosaic size. The size of the particle was calculated using Scherrer's formula (20) and it was found to be 27 nm, 20 nm and 14 nm for the bulk precipitated, conventional and microemulsion-derived ZnO nanoparticles, respectively.

Table 2 shows comparison of selected physical properties of ZnO prepared by three different methods. The highest surface area of ZnO nanoparticles corresponds to its smallest particle size.

TABLE 2

Comparative Study of BET Surface Area, ESD* and XRD Size of ZnO Particles

| Method of Synthesis	BET Surface Area	ESD	XRD Size
Bulk Precipitation	12.1 m^2/gm	87 nm	27 nm
Conventional powder	25.4 m^2/gm	43 nm	20 nm
Microemulsion	26.4 m^2/gm	40 nm	14 nm

* Equivalent Spherical Diameter

The advantage of using the nanoparticulate precursors obtained from microemulsions becomes evident when we compare the SEM micrographs of the sintered disks of different ZnO samples. They are strikingly different for all the three samples. The SEM micrographs clearly show the microstructural homogeneity and remarkably dense mode of packing of grains in disks of ZnO nanoparticles with minimum porosity, thus accounting for their highest conductivity, highest density and highest surface area as compared with those of larger ZnO particles, Fig. 2.

The quality of intergranular contacts for the three methods are indicated in the logE *versus* logJ curves for the pure ZnO sintered compacts as shown in Fig. 3. The better intergranular contacts are indicated by the higher conductivity of the microemulsion-derived sample.

The electrical properties can be correlated with the microstructure of the disks. Pure ZnO is a non-stoichiometric *n*-type semiconductor with a linear I-V behavior. To increase the efficiency of the varistor in high discharge current applications (like lightning protection or surge suppression) about six to seven orders decrease in grain resistivity is required in a narrow band of (clamping) voltage for the doped material.
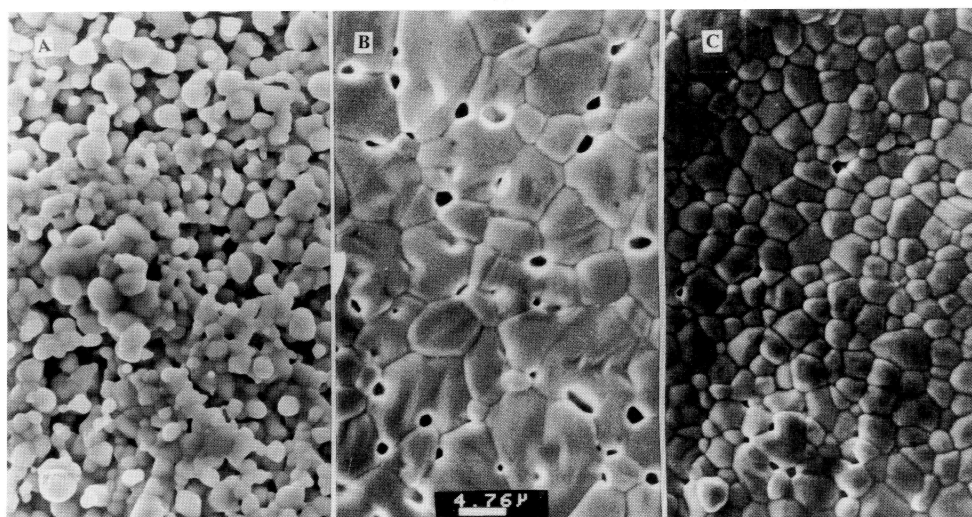
FIG.2
Scanning Electron Micrographs of ZnO disks sintered at 1200°C for 2h prepared by
(A) Bulk precipitation (B) Conventional powder (C) Microemulsion synthesis.
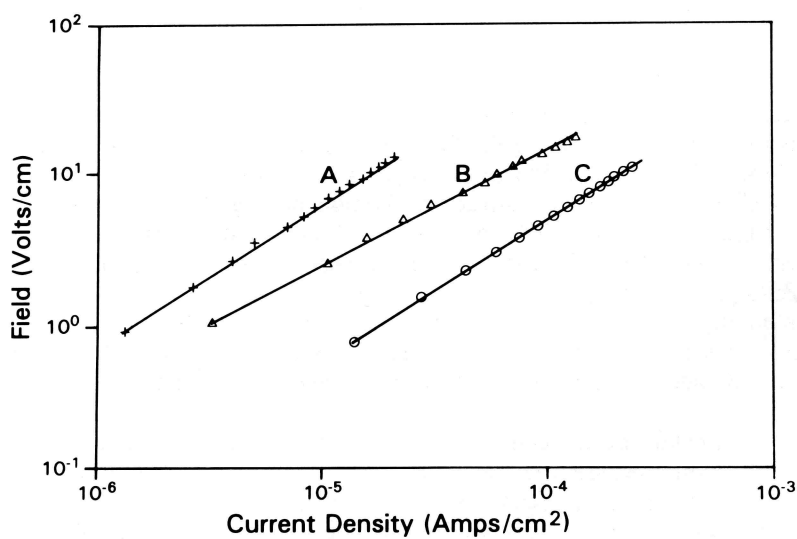
FIG.3
Results of Voltage - Current measurements for pure ZnO sintered compacts prepared by
(A) Bulk precipitation (B) Conventional powder (C) Microemulsion synthesis.

A final word about the quality of the microstructure of the doped ZnO disks. Fig.4 shows a typical SEM picture. The grains are equiaxed and the intergranular phases do not show any contrast at the magnification used. It is known that there are four types of intergranular phases present (21). Half of these in voltage biased regime are "good" (that is, show the characteristic Schottky barrier height) while the remaining half are "bad" (show very small barrier voltage). This has been amplified in ref. 22.
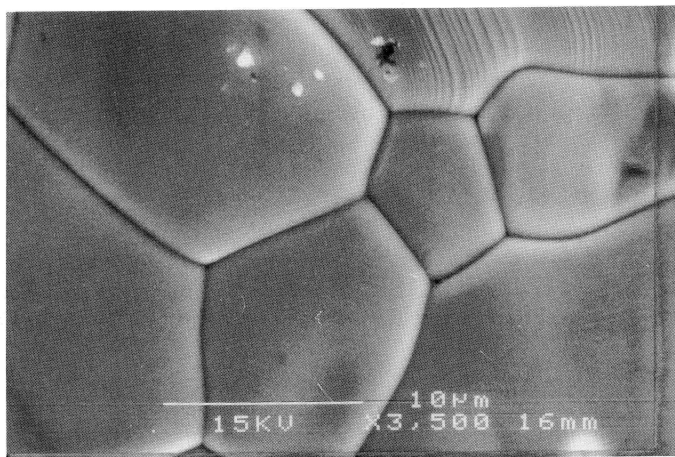

FIG.4
Scanning Electron Micrograph of sintered disk of ZnO
doped with 0.75 mol% Bi_2O_3 sintered at 1192°C for 16 h.

Conclusions

Careful varistor studies and quality applications require materials with strict control of homogeneity, particle size and shape. ZnO has an open hexagonal structure, allowing vacant sites for a number of tetrahedrally and octahedrally coordinated dopants. The most common excess is a metal in the interstitial sites, leading to an n-type semiconductor with a band gap of about 3.3 eV. Thus, deep-level traps are possible as well as donor-like and acceptor-like sites are possible, leading to rich variety of studies. This makes it compelling that the microstructure be well controlled. A single large particle or void resulting from a non-homogeneous particle size distribution may not be eliminated during sintering and may become the critical flaw, affecting electrical property.

A new process for the synthesis of ZnO nanoparticles by the microemulsion method has been developed. The optimized microemulsion system consisted of the surfactant cetyl trimethyl ammonium bromide, 1-butanol as cosurfactant, n-butane as continuous oil phase and aqueous solution as the dispersed phase. The microdroplets act as constrained microreactors for the precipitation reaction. These ultrafine precursor powders result in highly dense zinc oxide nanoparticles with narrow size distribution of nanometer dimensions. Critical study of the grain size dependence of electrical properties is carried out.

A comparison of properties for ZnO specimens using same purity of materials from the chemical, conventional and microemulsion routes showed that the microemulsion

synthesis yields zinc oxide nanoparticles which show largest surface area, highest density and maximum conduction at a particular voltage. SEM micrographs clearly show the distinct changes in packing nature of these particles. Our results highlight the potential of adopting microemulsion mediated process for synthesizing precursors for ZnO nanoparticles which is the major constituent of ZnO varistors.

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