Effect of process variables on the grain growth and microstructure of ZnO–Bi$_2$O$_3$ varistors and their nanosize ZnO precursors

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(Received 8 March 1994; accepted 18 October 1994)

The basic building block of the ZnO varistor is the ZnO grain formed as a result of sintering. Nanosized ZnO particles are prepared by carrying out the reaction in the controlled size nanoreactors—the droplets of microemulsions. Chemical doping of the ZnO nanoparticles provides ZnO-based ceramic varistors displaying superior varistor properties. These varistors show a higher value of the nonlinear coefficient, lower leakage current, and higher critical electric field value as compared to those for conventional samples in their log $E$ versus log $J$ curve. The present work has also been aimed at studying the effect of processing variables such as sintering temperature and duration on the microstructure and grain growth of ZnO nanoparticles and ZnO–Bi$_2$O$_3$ ceramics. The activation energy calculated from this data is found to be 175 kJ/mol for pure ZnO. For Bi$_2$O$_3$-doped ZnO, the activation energy is found to decrease considerably (~148 kJ/mol). All these advantages are due to greater structural homogeneity, smaller particle size, higher surface area, and higher density of the ZnO nanoparticles which are precursors for ZnO varistors, as compared to coarser particles for making varistors.

I. INTRODUCTION

Zinc-oxide-based varistors have found numerous applications as voltage regulators and transient voltage suppressors in electronic devices and in lightning strikes. In operation, the varistor is connected between the power source and the ground. When the electric field exceeds the switching field, $E_c$, the surge is carried away through the varistor, thus protecting the circuit or the power utility. It is, therefore, desirable to control varistor characteristics in order to optimize specific protection needs and device size requirements. Numerous investigators have studied the effects of processing and microstructure on electrical conduction in ZnO varistors.

Figure 1 shows the current-voltage ($I$-$V$) curve of a typical varistor showing three distinct regions: (i) Low-current linear region: The $I$-$V$ characteristic is ohmic in this region ($<10^{-4}$ A/cm$^2$) and is called the prebreakdown region. It determines the watt-loss and, hence, the operating voltage during the steady application of external voltage. (ii) Intermediate nonlinear region: The most significant feature of ZnO varistor is depicted by this region wherein the device conducts an increasingly large amount of current for a small increase in voltage. It determines the clamping voltage upon application of a transient surge. (iii) High-current upturn region: In this region ($>10^3$ A/cm$^2$), the $I$-$V$ characteristic is again linear, the voltage rising faster with current, showing ohmic behavior. It exceeds the limiting condition for protection from high current surges.

Varistor applications take advantage of all the regions of the $I$-$V$ curve. The most desirable device should have a high value of nonlinear coefficient, an acceptable rating of nonlinear voltage, a low value of leakage current, a long varistor life, and a high energy absorption capability. The nonlinear portion of the curve has been defined by the equation,

$$ I = CV^a, $$

![FIG. 1. I-V curve of a ZnO varistor.](image)

where \( C \) is a material constant, \( I \) is the current, \( V \) is the voltage applied to the varistor, and \( \alpha \) is the nonlinearity coefficient.

Low voltage varistors often suffer from a large spread in the current/voltage characteristics due to discontinuously grown, inhomogeneous microstructures. It is reported\(^3\) that high local currents and overload are caused by single large grains which give rise to rapid degradation of varistor in electrical operation. Hence, a careful control of microstructures of the \( \text{ZnO} \) material is needed to obtain correct values for the breakdown voltage and nonlinearity exponent.

Several workers\(^4-7\) have found ways of increasing homogeneity and inhibiting grain growth in sintered disks. Hennings \textit{et al.}\(^4\) have shown that addition of seed grains to the ceramic powder is an effective means of controlling the final grain size and electrical properties, narrowing them around a mean value. Rahaman \textit{et al.}\(^5\) have proposed that the addition of aluminum at the 125 ppm level inhibits grain growth. Varistors used in high voltage applications need to have relatively smaller size grains (5 to 10 \( \mu \text{m} \)) so as to keep the varistor volume low, enhancing the efficiency of cooling techniques. This is based on the fact that the voltage drop across each grain boundary is about 3.2 V. Hot-pressing techniques have been successfully employed to reduce grain size and porosity.\(^6\) Amiji \textit{et al.}\(^7\) have suggested the need for a homogeneous distribution of properties to control thermal stresses arising from variations in resistance, and, therefore, localized heat buildup. To achieve a uniform sintered microstructure, uniformly packed particles with a narrow size distribution are needed.\(^8\) ZnO nanoparticles of very fine particle size can be achieved by synthesizing them in the constrained nanoreactors of microemulsion droplets.

Microemulsions are transparent dispersions containing two immiscible liquids (e.g., oil and water) stabilized by a surfactant. Operating in the appropriate region of phase diagram allows one to choose a region where the spherical droplets are of 10–50 nm diameter that are generally obtained on mixing the two immiscible liquids. In water-in-oil, microemulsions, the aqueous phase is dispersed as nanosize droplets surrounded by a monolayer of surfactant molecules in the continuous hydrocarbon phase.\(^9\) The aqueous cores of microemulsions containing soluble metal salts are used as nanoreactors for the synthesis of finely divided \( \text{ZnO} \) particles. The rate of coalescence of two microemulsion droplets controls the rate of reaction. Nanoparticles of Pt, Pd, Rh, and Ir have been synthesized using this approach.\(^11\) Since then many ultrafine particles such as \( \text{BaCO}_3\), \( \text{CaCO}_3\), \( \text{AgCl} \) and \( \text{AgBr} \), \( \text{BaF}_{2} \), \( \text{BaO} \), \( \text{Y}_2\text{O}_3 \), and \( \text{SiO}_2 \) have been prepared using the microemulsion media. We used nanoparticles of \( \text{ZnO} \) for varistor fabrication, and they showed higher bulk density and greater uniformity. The sintered density is dependent on the average particle size, being greater for finer particles. It is also known that samples with small grain size withstand relatively higher energies as these samples have a larger number of grain boundaries. The reduction in particle size will improve the overall properties of a varistor. Nanoparticles yield a narrow grain size distribution and excellent stability against grain growth. They sinter at a lower temperature than coarser grained ceramics, retaining their ultrafine grain sizes after sintering to full density and exhibit superior mechanical properties as well.\(^8\)

The properties of ceramic products produced by the conventional ceramic fabrication procedures are known to be influenced by processing variables such as powder preparation including initial heat treatment, average initial particle size, compacting techniques, sintering, and sintering heat treatments. Since \( \text{ZnO} \) varistors are also prepared by the same technique, it is logical to expect that their properties are also controlled by the processing parameters mentioned above. It is known that the width of the grain boundaries decreases with increasing sintering temperature or time.\(^2\) Barriers to electrical conduction in a \( \text{ZnO} \) varistor material are formed during cooling from the sintering temperature. The tunneling effect can be apparent when the width of the boundaries decreases, and the electrical properties can be better. It also contributes to good \( \text{ZnO} \)--\( \text{Bi}_2\text{O}_3 \)--\( \text{ZnO} \) contacts, minimizing interface energy to produce better electrical properties.\(^17\) Chen \textit{et al.}\(^18\) prepared the \( \text{ZnO} \) varistors by conventional ceramic fabrication technique and studied the effect of sintering time on the depression angle \( (\theta_1) \) and the relaxation time \( (\tau_3) \). Both decrease with increasing sintering time, implying that spatial nonuniformity of intrinsic defects which existed near the grain boundary decreases with increasing sintering time. Since the reduction of surface area is the principal driving force for sintering, a powder with a large surface area and uniform particle size, which can be produced by the microemulsion method, is an attractive candidate for sintering studies.

The phenomenon of grain growth in pure and doped \( \text{ZnO} \) has been studied earlier for the conventionally prepared samples.\(^19\) For pure \( \text{ZnO} \) the activation energy was found to be reported in the range from 213 to 409 \text{kJ/mol}, and for the \( \text{ZnO}--\text{Bi}_2\text{O}_3 \) system it was found to be 150 \text{kJ/mol}.\(^20\) We have studied in this paper, grain growth of pure \( \text{ZnO} \) nanoparticles prepared in microemulsion media, as well as \( \text{ZnO} \) nanoparticles with \( \text{Bi}_2\text{O}_3 \) additions of 0.5 to 4 wt. % for varying sintering temperatures. The dopant was added in a manner to ensure homogeneity as reported earlier.\(^21\) The grain growth can be expressed by the kinetic grain growth equation:

\[
G^n - G_0^n = \frac{K_0}{Q} \exp\left(-\frac{Q}{RT}\right),
\]
where $G$ is the average grain size at the time $t$, $G_0$ is the initial grain size, $n$ is the kinetic grain growth exponent, $K_0$ is a constant, $Q$ is the activation energy, $R$ is the gas constant, and $T$ is the absolute temperature.\textsuperscript{22}

II. 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 I).

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 droplets. The particles thus prepared in the constrained nanoreactors of microemulsion droplets are fairly uniform, homogeneous, and have higher surface area with very small particle size (5 nm). The various steps involved in the preparation of ZnO nanoparticles in microemulsion media are shown in Fig. 2. The details of the process have been described by the authors in their earlier work.\textsuperscript{21}

Before the pressing operation, the powder was characterized with respect to particle size using XRD analysis and BET surface area measurements. For studying the effect of processing parameters, ZnO disks of 1 cm diameter were prepared by pressing the ZnO nanoparticles under a pressure of 70 MPa. These disks were then sintered in air at temperatures of 900, 1000, 1100, and 1200 °C, keeping the sintering duration fixed for 2 h, to study the effect of sintering temperature on the morphology and electrical properties of disks of ZnO nanoparticles. Then the effect of sintering duration was studied by holding the sample at 1200 °C for 0.5 h, 1 h, 2 h, 6 h, 12 h, and 24 h in air. The rate of heating (3 °C/min) and cooling (10 °C/min) during sintering was the same for all specimens. However, even other factors were kept exactly similar in all the cases.

For electrical measurements, ohmic contacts were applied to both surfaces of the disks by coating with colloidal silver paint. Standard $V-I$ measurements were carried out using a stabilized dc power source in current range up to 10 mA. The microstructure and grain size distribution studies were carried out on a JEOL 6400 scanning electron microscope. The grain sizes were directly measured from photomicrographs of the etch samples observed by scanning electron microscopy. The average grain size $G$ was obtained as $G = 1.56 L$, where $L$ is the average grain boundary intercept length of 50 random lines across the micrographs.\textsuperscript{23}

III. RESULTS AND DISCUSSION

The present synthesis method for ZnO nanoparticles in microemulsion (ME) media is promising because the resulting particles are markedly smaller, having higher surface area, lower XRD size (from XRD line broadening), and higher density as compared to those typical obtained in conventional aqueous or organic solutions (Table II). It may, however, be noted that the solid state decomposition of ZnCO$_3$ (see label, Conventional Powder, in Table II) also leads to ultrafine particles, as this study has been reported in Ref. 21. The ME-derived powders give sintered disks that form grains with narrow grain size distribution, are equiaxed, and have inherent stability against grain growth.

The microstructures developed during sintering have an important effect on the electrical properties of ZnO varistors. The surge stability and energy absorption

<table>
<thead>
<tr>
<th>TABLE I. Composition of the microemulsions.</th>
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<tbody>
<tr>
<td><strong>Microemulsion I</strong></td>
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<tr>
<td>Aqueous phase</td>
</tr>
<tr>
<td>Surfactant</td>
</tr>
<tr>
<td>Co-surfactant</td>
</tr>
<tr>
<td>Oil phase</td>
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</tbody>
</table>

the varistor increase upon sintering. It is reported that permanent changes occur in the prebreakdown region of the I-V curve due to sintering.\textsuperscript{1} Since the major degradation of the varistor occurs in the prebreakdown region with the upturn region remaining unaffected by stressing, we thought it worthwhile to study the effect of sintering duration and temperature on pure undoped ZnO disks prepared from ZnO nanoparticles. It was observed that on increasing the sintering time or temperature, the electrical properties are found to improve. The spatial nonuniformity of intrinsic defects which existed near the boundary decreases with increasing sintering time. The longer sintering time or higher sintering temperature makes most of the ZnO–ZnO junction into direct contacts and minimizes the interface energy. For this reason these samples can exhibit higher electrical conduction. However, it is unique that they can also retain their ultrafine grain sizes after sintering to full density. There is no significant change in density of the sintered disks relative to sintering time or temperature.

A recent report\textsuperscript{24} indicates that the dopant concentrations we have used are above the carefully determined solidus boundary in the ZnO–Bi$_2$O$_3$ system phase diagram. Thus, the sintering kinetics would be determined by the liquid state sintering since all the dopant concentrations are in the liquid state above the eutectic temperature of 740 °C.\textsuperscript{25} Besides, we have succeeded in maintaining a relatively low average grain size (this paper and Ref. 21 which reports on varistors with the full complement of dopants) without the need for hot pressing as has been done for the sol-gel-derived varistors.\textsuperscript{26} It may be noted that Halle et al.\textsuperscript{27} have reported that the varistors made from powders derived from aqueous precipitation of ZnO as well as from dry-mixed ZnO powders with all the additives lead to calcined powder which lead to considerably larger initial particle size (3 μm). On the other hand, Senda and Brad\textsuperscript{23} report grain sizes of about 25 μm when compared with the sintered microstructures for the same temperature and time as ours. However, it may be noted that their presintering particle size was an average of about 0.1 μm.

Close examination of the photomicrographs of pure and doped ZnO reveals that the grain size increases proportionately with sintering duration and temperature. SEM micrographs showing grain growths of pure ZnO

<table>
<thead>
<tr>
<th>Method of synthesis</th>
<th>BET surface area</th>
<th>ESD</th>
<th>XRD size</th>
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</thead>
<tbody>
<tr>
<td>Bulk precipitation</td>
<td>12.1 m$^2$/gm</td>
<td>87 nm</td>
<td>27 nm</td>
</tr>
<tr>
<td>Conventional powder (on decomposition of carbonate)</td>
<td>25.4 m$^2$/gm</td>
<td>43 nm</td>
<td>20 nm</td>
</tr>
<tr>
<td>Microemulsion</td>
<td>26.4 m$^2$/gm</td>
<td>40 nm</td>
<td>14 nm</td>
</tr>
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</table>

\textsuperscript{a}Equivalent spherical diameter.

![FIG. 3. Photomicrographs of disks of pure ZnO nanoparticles prepared in microemulsions and sintered at (A) 900 °C, (B) 1000 °C, (C) 1100 °C, and (D) 1200 °C for 2 h in air.](image-url)
sintered at 900 °C through 1200 °C are shown in Fig. 3. The kinetic grain growth equation can be plotted in the form:

$$\log(G^a/t) = \log K_0 - 0.434(Q/RT)$$

From the slope of the log (grain size) versus log (time) plot, which is $1/n$, the grain growth kinetic exponent $n$ is readily determined. The process follows the standard phenomenological kinetic grain growth with a kinetic grain growth exponent of 2.6 (Fig. 4). Figure 5 illustrates the Arrhenius plot constructed from the previous data in which log($G^a/t$) is plotted versus the reciprocal of the absolute temperature (1/T). The slope of this plot yields the apparent activation energy for the grain growth process and is found to be 175 kJ/mol.

The ZnO grain growth in the binary ZnO–Bi$_2$O$_3$ system was also studied. The photomicrographs of these specimens fired at 1192 °C for varying sintering duration (Fig. 6) and for varying sintering temperature from 900 °C through 1200 °C for a fixed duration of 2 h are shown in Fig. 7. There is a significant enhancement in grain growth in these systems as compared with the growth in pure ZnO. This is perhaps due to the formation of a Bi$_2$O$_3$-rich liquid phase at the grain boundaries, the increasing the grain boundary mobility and the rate of grain growth. Grain growth of these specimens in the form of log (grain size) versus log (time) plots is depicted in Fig. 8. The average grain growth kinetic exponent $n$ was found to be 3.5. Using this average $n$ value, the Arrhenius plots were constructed, and the activation energy derived from the slope of the Arrhenius plot 148 kJ/mol (Fig. 9). The reduction in activation energy upon doping ZnO with Bi$_2$O$_3$ may be due to the physical processes involved during sintering. It appears that the...
content of Bi$_2$O$_3$ does not affect the value of activation energy (148 ± 5 kJ/mol).

IV. SUMMARY AND CONCLUSIONS

Zinc oxide varistors are polycrystalline electronic devices whose pronounced nonohmic current-voltage characteristics are derived from the electrical properties of its grain boundaries. Microstructural homogeneity is a key parameter to control the ohmic to nonohmic behavior of varistors. ZnO particles prepared in microemulsion media are uniform, dense, and nanosized, having high surface area and surface free energy which can be sintered to near-theoretical density at low sintering temperature and time. To optimize nonlinearity thermal conduction, and strength, a powder that can be densified quickly with minimum grain growth is desired. Electrical properties can be carefully tailored for a specific application by controlled addition of dopants. Variation of processing parameters also has a significant influence on the microstructure and varistor properties. The grain growth phenomenon in pure ZnO and Bi$_2$O$_3$ doped ZnO has been studied and the activation energy found to be 175 kJ/mol for pure ZnO and 148 kJ/mol for binary ZnO–Bi$_2$O$_3$ systems. Since grain size is controlled by sintering parameters, the desired critical voltage of a varistor for a given application can be adequately controlled through varistor processing.

ACKNOWLEDGMENT

The authors gratefully acknowledge the research support for their project from Electric Power Research Institute (EPRI) (Grant No. RP8001-11).

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