

Direct-Write Fabrication of Zinc Oxide Varistors

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Zinc oxide (ZnO)-based pastes with tailored rheological properties have been developed for direct-write fabrication of thick-film varistor elements in highly integrated, multifunctional electroceramic devices. Such pastes exhibited pseudo-plastic behavior with a low shear apparent viscosity of roughly 1×10^4 Pa·s. Upon aging, the pastes attained printable, steady-state viscosities of approximately 3×10^2 Pa·s at 10 s^{-1} . Square and rectangular elements were patterned on dense alumina substrates and sintered at varying temperatures between 800° and 1250°C . Varistor elements fired at 900°C exhibited nonlinearity coefficients ($\alpha = 30$) that were equivalent to high-density (>95%) varistors formed by cold isostatic pressing at 100 MPa (15 ksi) of a similar chemically derived powder heat-treated under analogous conditions.

I. Introduction

FABRICATION of advanced electrical ceramic devices is commonly achieved via a multilayer build sequence that utilizes thick film process technologies such as tape casting and screen-printing.^{1–8} As device complexity increases, the need for alternate fabrication methods that offer a simple and rapid means of integrating multiple materials in 3-D architectures has intensified. Direct-write fabrication techniques, such as the micropen system, allow integrated multifunctional, multimaterial electroceramic devices to be produced in an agile fashion.^{9,10} In this method, a thin cylindrical extrudate (minimum diameter $\approx 25 \mu\text{m}$) is deposited in a precise pattern onto a substrate via computer-aided design (CAD) instruction. Complex, 3-D architectures can be constructed in a layer-by-layer build sequence from individual layers containing multiple materials. Although drying of as-printed layers is required prior to deposition of additional layers, this direct-write approach yields significant advantages over the conventional method for producing multilayer devices, such as those based on lamination of tape-cast layers with screen-printed elements, including the ability to modify patterned designs on-line during printing and to incorporate multiple materials in individual layers.

The rheological requirements of thick film pastes for micropen printing and screen printing are nearly identical.^{7–9,11–17} Hence, commercially available screen printing pastes (e.g., silver–palladium conductor, ruthenium oxide resistor, and dielectric pastes) can be readily utilized in this direct-write approach. However, there is a need to develop rheologically tailored, cofireable thick

film pastes of functional ceramic materials.^{18–22} In a companion paper,²³ we described the protocol used to develop appropriate inks for direct writing of high-performance PNZT capacitor elements.

Here, we demonstrate the generality of our approach by developing ZnO-based pastes with tailored rheological properties for micropen fabrication of varistor elements. Such elements are useful for applications ranging from voltage surge protectors to power switches. In this work, we first examined the influence of dispersant concentration and aging time on the rheological behavior of ZnO suspensions. We then characterized the microstructural evolution and current–voltage characteristics of sintered 20 to 60 μm thick, single-layer, varistor devices.

Zinc oxide varistors are complex, polycrystalline ceramics with superb voltage regulation and transient voltage suppression capabilities. The electrical response²⁴ of varistor elements depends on the magnitude of applied electric field. For fields that are below their characteristic “switching” field, varistors exhibit large resistivities, typically greater than $10^9 \Omega\cdot\text{cm}$, and are essentially ohmic. Grain boundary regions within the varistor are highly insulating at low voltages, with the major phase ZnO grains have resistivities on the order of $10 \Omega\cdot\text{cm}$. As the applied field approaches the switching field, the current density increases in a highly nonlinear fashion. Several mechanisms have been proposed to describe the highly nonlinear conduction across grain boundaries under these conditions including Fowler–Nordheim tunneling²⁵ and thermionic emission over electrostatic barriers²⁶ coupled with hole generation²⁷ leading to accelerated collapse of the grain boundary barrier with increasing field.

Macroscopically, the nonlinear varistor response is given by following power law relationship:

$$J = k(E)^\alpha \quad (1)$$

where J is current density, E is electric field, k is an inverse resistivity parameter defined for a given current density, and α is the nonlinearity coefficient. The nonlinearity coefficient is calculated by

$$\alpha = \log(J_2/J_1) / \log(E_2/E_1) \quad (2)$$

For which $J_2 > J_1$ and $E_2 > E_1$. Comparisons of varistor switching fields and nonlinearity coefficients were made for direct-write varistor elements fired at different temperatures and for bulk varistors²⁸ formed by cold isostatic pressing. Specifically, the switching field, defined as the electric field at $1 \text{ mA}/\text{cm}^2$, and the nonlinearity coefficient, α , measured between 1 and $5 \text{ mA}/\text{cm}^2$, were the two primary electrical properties considered in our study.

II. Experimental Procedure

(I) Materials System

Zinc oxide varistor powder, derived via a hydroxide/oxalate coprecipitation method followed by a precipitation/hydrolysis of Bi to the powders using an acidic solution,^{29,30} served as the ceramic phase in this study. The chemical composition of this

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powder is provided in Table I. Bi_2O_3 , CoO , and MnO were added on the order of 0.25 to 0.6 mol% to enhance powder sinterability and electrical properties. Na (300 ppm) and Al (130 ppm) were also purposefully added for improved degradation resistance^{31,32} and controlled grain size,³³ respectively. The varistor powder used in this study has a mean diameter of 2.7 μm , as determined by particle size analysis (Model CAPA 700, Horiba particle size distribution analyzer), and an apparent density of 5.63 g/cm^3 , as measured by helium pycnometry (Ultracycrometer 1000, Quantachrome Corp., Boynton Beach, FL). This powder consisted of primary crystallites on the order of 60 nm, which were allowed to form weak micrometer-sized agglomerates during precipitation to facilitate powder handling. Note, the calculated density assuming a two-phase mixture of ZnO and Bi_2O_3 using lattice parameters determined by X-ray diffraction analysis is 5.67 g/cm^3 . In our companion paper,²³ a suitable organic vehicle was identified for microopen fabrication, which consisted of Menhaden fish oil as a dispersant, ethyl cellulose (EC) (Ethocel; Standard 10, Dow Chemical Corp., Midland, MI) as a binder, and α -terpineol (boiling point $\approx 220^\circ\text{C}$) (Aldrich Chemical Co., Milwaukee, WI) as a low-volatility solvent. The cellulose binder has a 48.0–49.5% ethoxy content and a molecular weight of approximately 10 500 g/mol.

(2) Sample Preparation

ZnO suspensions ($\phi_{\text{ZnO}} = 0.10$) were prepared by adding an appropriate amount of powder to an α -terpineol solution containing varying dispersant concentrations (1.0–5.0 wt% by weight of ZnO powder). These suspensions were then ball-milled for 12 h. After ball milling, the cellulosic binder was added at a volume fraction ($\phi_{\text{EC}}^{\text{soln}}$) of 0.05 in solution. These pastes were first mixed manually using a Teflon rod, followed by three-roll milling (Charles Ross and Son Co., Hauppauge, NY) (10 μm gap, four passes). Representative samples were characterized by stress viscometry and centrifugal consolidation (in the absence of cellulose binder additions). The former measurements allowed us to determine the optimal dispersant concentration, whereas the latter measurements allowed us to determine the maximum volume fraction, $\phi_{\text{ZnO}}^{\text{max}}$ of 0.33, for such systems by measuring their equilibrium sediment height. For direct-write fabrication of varistor elements, ZnO pastes ($\phi_{\text{ZnO}} = 0.30$, $\phi_{\text{EC}}^{\text{soln}} = 0.05$) were prepared at the optimal dispersant concentration of 3 wt% fish oil (by weight of ZnO powder) following this same procedure.

Chemically prepared ZnO varistor powders were formed into compacts for sintering by first uniaxial pressing at 14 MPa in a 1.5 cm diameter die. The 0.6 cm thick pressed compacts were then cold isostatically pressed at 100 MPa. These bulk chemically prepared varistors are termed cold isostatically pressed or CIP varistors in this paper. The varistor powders were pressed dry, with no binder or water added to aid compact formation and subsequent handling.

(3) Rheological Measurements

ZnO pastes were characterized using a controlled stress rheometer (Carri-med 50, Carri-med Corp. (now TA Instruments, New Castle, DE) in stress viscometry mode. The rheometer was fitted with either a double concentric cylinder (DG) or cone and plate geometry. The rheological behavior of ZnO pastes were measured

using a DG cell, which yielded a stress range of 1×10^{-4} – 1×10^1 Pa. The higher-viscosity ZnO pastes were characterized using a cone and plate geometry (cone diameter = 2.0 cm, cone angle = 0.5°), which yielded a stress range of 5×10^{-2} – 5×10^3 Pa. The rheological behavior of as-milled pastes was characterized first, followed by a series of measurements as a function of aging time. After a representative aliquot of paste was tested initially, the remaining paste was allowed to age undisturbed either under ambient conditions or at an elevated temperature ($T \sim 50^\circ\text{C}$). Subsequent aliquots were then removed and characterized at various time intervals. The apparent viscosity of each sample was measured as a function of shear stress in ascending order. All rheological measurements were carried out at 22°C . Given the low volatility of the solvent, no special precautions were necessary to prevent solvent evaporation during these measurements.

(4) Direct Fabrication and Component Properties

Varistor elements were prepared via computer-aided direct-deposition of ZnO pastes onto dense alumina (Coors Ceramic Co., Golden, CO) substrates using a commercial microopen system (Ohmcraft Inc., Pittsford, NY) fitted with a 4/3 pen tip (outer diameter = 4 mils; inner diameter = 3 mils).^{9,10} Single layer square components (25 mm \times 25 mm \times 0.030 mm) were fabricated for sintering studies, and multilayer rectangular components (1 mm \times 3.5 mm \times 0.060 mm, after firing) were produced for electrical measurements. Multilayer structures were deposited in a layer-by-layer build sequence in which individual layers (≈ 40 – $60 \mu\text{m}$) were allowed to settle (level) for 180–300 s under ambient conditions. Upon leveling, the layer(s) were dried at 110°C under vacuum (50.8 mmHg). Additional layers were then deposited on the as-dried films as needed for a given device. The surface topography and cross-sectional area of as-dried elements were profiled using laser profilometry (CyberScan Corba, Cyber Optics Corp., Golden Valley, MN), which revealed excellent thickness uniformity.

Representative ZnO samples were debinded at 450°C for 3 h at a heating rate of $2^\circ\text{C}/\text{min}$, and subsequently sintered at 800° , 850° , 900° , 1000° , or 1250°C in air.^{34–37} The soak time for all firing temperatures was 1 h with the exception of direct-write varistors fired at 1000°C that were subjected to a 4 h soak. The samples were cooled back to room temperature at a rate of $5^\circ\text{C}/\text{min}$. Fractured and polished surfaces of sintered ZnO samples were analyzed by scanning electron microscopy to evaluate their microstructural evolution.

DC voltage–current measurements were performed on electroded, multilayer ZnO varistor elements. Square silver electrodes (DuPont 7095 silver paste 7095) ($2 \times 2 \text{ mm}^2$) were either screen printed or hand painted using a mask on the top surface of each sample. The samples were then fired to 600°C for 0.5 h following identical heating and cooling rates to those specified above for the sintering process. Rounded tungsten or bronze probe tips (Model 725S semiconductor probes, Signatone, Gilroy, CA) were contacted to fired silver electrodes for electrical measurements. The electrical properties of varistor elements were probed over a range of current densities (i.e., from 1×10^{-7} to $5 \times 10^{-3} \text{ A}/\text{cm}^2$) using an electrometer (Model 619 Electrometer, Keithley, Cleveland, OH) to monitor current, a multimeter¹³ (Model No. 3478A, Hewlett-Packard, Palo Alto, CA) to monitor voltage and a power supply¹⁴ to apply voltage.

III. Results and Discussion

(1) Rheological Properties

The apparent viscosity (η_{app}) as a function of shear rate ($\dot{\gamma}$) for ZnO suspensions ($\phi_{\text{ZnO}} = 0.10$) with varying Menhaden fish oil (MFO) concentration (weight percent relative to powder mass) is shown in Fig. 1. The low shear viscosity, $\eta_{\text{app},0}$, and the degree of shear thinning decreased with increasing dispersant concentration, indicative of enhanced suspension stability. Suspensions containing dispersant concentrations of 3.0 wt% or higher were most stable, exhibiting the least degree of shear thinning behavior. The

Table I. Chemical Composition of ZnO Powder

	Composition
ZnO	98.94 mol%
CoO	0.25 mol%
MnO	0.25 mol%
Bi_2O_3	0.56 mol%
Al	130 ppm
Na	300 ppm

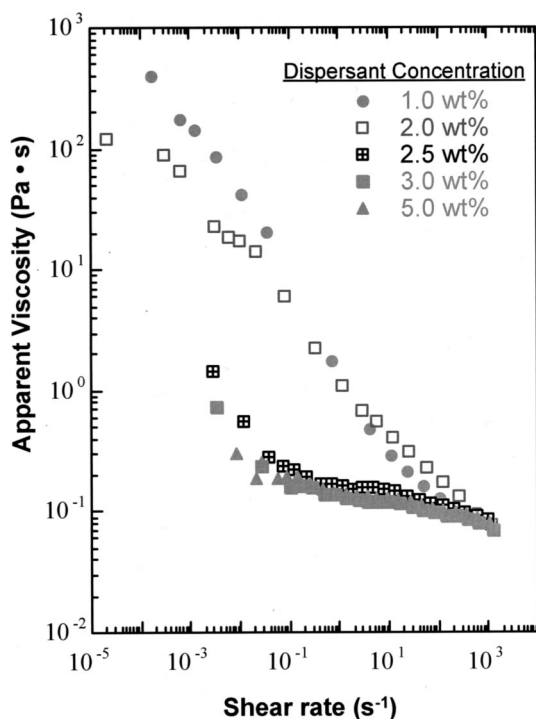


Fig. 1. log-log plot of apparent viscosity as a function of shear rate for ZnO suspensions ($\phi_{ZnO} = 0.10$) with varying Menhaden fish oil (MFO) concentration (weight percent dispersant relative to powder mass).

optimal dispersant content was found to be 3.0 wt% MFO for these suspensions. The apparent viscosity as a function of shear rate for representative ZnO pastes ($\phi_{ZnO} = 0.30$, $\phi_{EC}^{soln} = 0.05$, and 3 wt% MFO) under varying aging conditions is shown in Fig. 2. All pastes exhibited pseudoplastic behavior. Pastes held at room temperature exhibited little change in their rheological behavior with aging time. In comparison, samples aged for 96 h at elevated

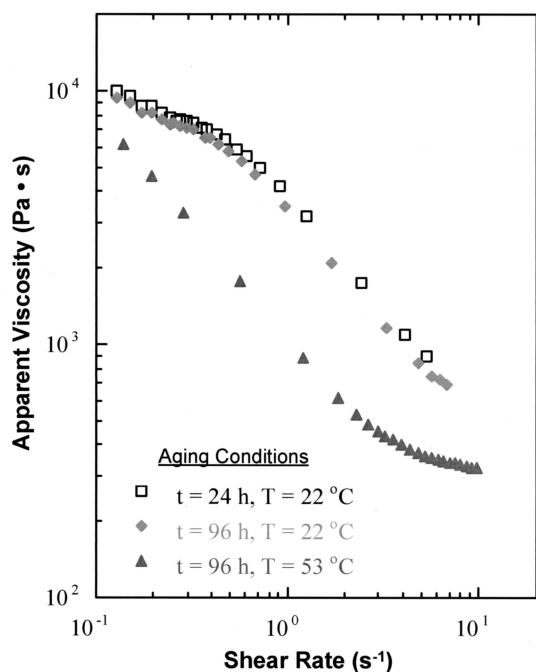


Fig. 2. log-log plot of apparent viscosity as a function of shear rate for ZnO pastes ($\phi_{ZnO} = 0.30$, $\phi_{EC}^{soln} = 0.05$, and 3 wt% MFO dispersant) aged under varying conditions.

temperatures ($\sim 50^\circ\text{C}$) exhibited a significant decrease in their low shear viscosity relative to samples aged under ambient conditions for the same time period. In related work, Morissette *et al.*²³ demonstrated that aging times of nearly 50 days were required under ambient conditions for PNZT thick film pastes (in the same organic vehicle) to approach steady-state flow behavior. The observed acceleration at elevated temperatures suggests that adsorption kinetics likely play an important role in this process. Possible rate-limiting steps include either diffusion of dispersant species to the powder surfaces or their subsequent adsorption onto such surfaces.

(2) Electrical Properties of Sintered Varistor Elements

Direct-write varistors fired at 900°C have nonlinearity coefficients (Fig. 3) that compare favorably with bulk, isopressed (100 MPa) ZnO varistors.²⁸ Both direct-write and cold isostatically pressed (CIP) varistors were formed from similar chemically derived powder. The isopressed and direct-write varistors were identical in composition, with the exception that the isopressed varistors contained only 30 ppm Na. Current density versus electric field characteristics are shown in Fig. 3 for the direct-write varistors and CIP bulk varistors fired at 900° and 1000°C, respectively. Interestingly, the nonlinearity coefficients for the 900°C direct-write varistor were more similar to those of the 1000°C bulk varistor than the 900°C bulk varistor. Nonlinearity coefficients of 30, 16, and 6 were measured for the 900°C direct write, 1000°C CIP bulk varistor, and 900°C CIP bulk varistor, respectively. The difference in nonlinearity coefficient can be influenced by the higher Na content for the direct-write materials. Na doping lowers the eutectic melt temperature of bismuth oxide, leads to more uniform distribution of Bi throughout the varistor microstructure,³⁸ and alters the defect chemistry³² at the grain boundaries. All three effects of Na doping will increase the percentage of grain boundaries with highly nonlinear electrical behavior, thereby enhancing the macroscopic nonlinearity coefficient.

The electric switching fields measured at 1 mA/cm² were 11.9, 3.5, and 4.2 kV/cm for the 900°C direct write, 1000°C CIP bulk varistor, and 900°C CIP bulk varistor, respectively. The larger electric field exhibited by the direct-write varistor can in part be attributed to the soak time (1 h compared to 16 h for the isopressed material). The shorter soak time for the direct-write varistor will lead to smaller grain size, a larger number of grain boundaries per unit thickness, and greater switching fields. Typically, there is a voltage drop of approximately 3 V per grain boundary in ZnO

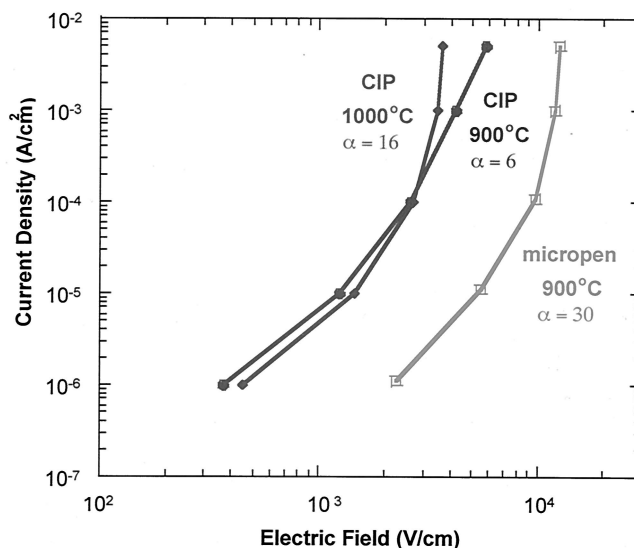


Fig. 3. log-log plot of current density as a function of applied electric field for cold isostatically pressed varistors fired at 900° and 1000°C and direct-write varistor fired at 900°C.

varistors,^{25,39} so the greater the number of grain boundaries per unit thickness, then the greater the switching field. Microstructural analyses presented later in this paper support the premise of greater switching field for smaller grain size varistors.

Interestingly, varistor components directly fabricated from ZnO varistor pastes exhibited highly nonlinear current–voltage characteristics for only the 900°C firing temperature. A plot of the nonlinearity coefficient, α , measured from 1 to 5 mA/cm², versus firing temperature is shown in Fig. 4, which dramatically illustrates the narrow firing range behavior. Specifically, varistors fired only 100°C above and 50°C below the best firing temperature of 900°C had substantially lower nonlinearity coefficients, 1.7 and 5, respectively. Although even our highest α value of 30 is low compared to commercial ZnO varistors (for which $\alpha \sim 50$), such components are typically fired at temperatures on the order of 1300°C and have a much lower field (1.6 kV/cm compared to 12 kV/cm at 1 mA/cm²) than those studied here. An α value on the order of 30 is quite acceptable for many applications, especially when combined with the 6 times higher field of operation for varistors derived from chemically prepared powders compared to those from conventional mixed oxide powders. The size of varistors for integrated ceramics packaging is reduced since the component length required to regulate a given voltage is 6 times less for the higher switching field chem-*prep* varistors.

The current density versus electric field characteristics for micro-pen varistors fired at 800°, 900°, 1000°, and 1250°C are shown in Fig. 5. Electric switching field decreased with increasing firing temperature and larger grain size as expected. Switching fields ranged from 15 kV/cm for the 800°C firing to 0.060 kV/cm for the 1000°C firing. The nonlinearity coefficient decreases from 30 for the 900°C firing to 1 for the 1250°C firing and to 3 for the 800°C firing. An $\alpha = 1$ indicates purely ohmic behavior and indicates that essentially all of the Bi has been removed from the ZnO grain boundary regions. Although the 1250°C varistor does not exhibit a switching field, the field at 1 mA/cm² for this resistor is 0.0025 kV/cm. This field value corresponds to a resistivity of $2.5 \times 10^3 \Omega\cdot\text{cm}$, which is not an unreasonable value for polycrystalline ZnO ceramics. Once again, it is striking that direct-write varistors with useful voltage regulation properties are only produced over an extremely narrow firing temperature range (less than 100°C).

(3) Microstructural Properties of Direct-Write Varistors

Microstructural analysis (SEM imaging combined with EDS measurements) elucidated the reasons for the narrow firing temperature range for good varistor performance for direct-write ZnO

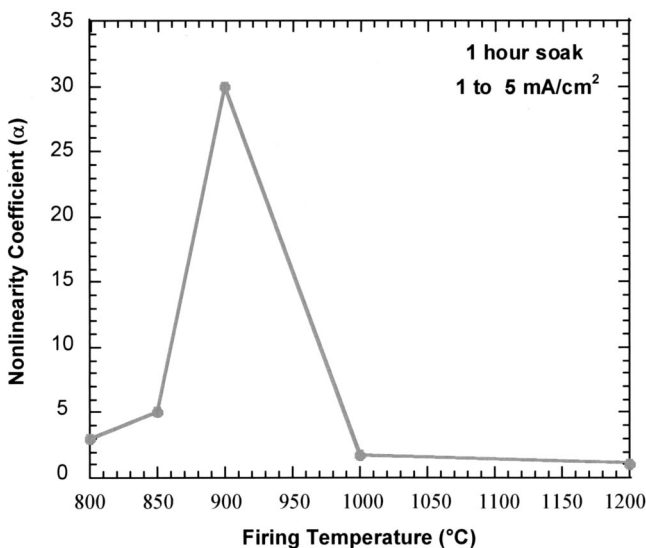


Fig. 4. Nonlinearity coefficient versus firing temperature for direct-write ZnO varistors.

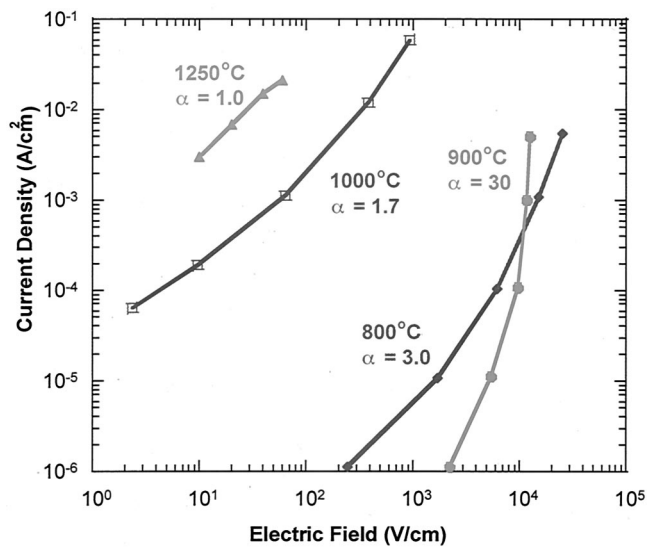


Fig. 5. log–log plot of current density (J) as a function of applied electric field of direct-write ZnO varistors sintered at varying temperatures.

varistors. At lower sintering temperatures (800° and 850°C), samples did not densify to an appropriate level to yield a high volume fraction of Bi-doped grain boundary regions resulting in inferior J – E response. An open, fine grained ZnO structure was observed for these direct-write elements, as shown in Fig. 6(a). In contrast, CIP bulk ZnO varistors fired at these temperatures achieve greater than 85% of theoretical density. The low packing density ($\sim 30\%$) of the direct-write elements relative to the CIP bulk varistors (green densities of $\sim 58\%$) surely contributes to differences in their apparent density and electrical behavior. We postulate that sintering temperatures higher than 1000°C resulted in lower nonlinearity coefficients due to loss of Bi from the ZnO varistor structure. Figure 6(b) provides some support for this premise, as relatively large 5 to 10 μm grains with significant intragranular fracture are observed for the 1250°C varistor. ZnO varistors with Bi at the grain boundaries have a strong tendency to fracture intergranularly. Further, no Bi-rich phases were detected at three-grain intersections for the 1250°C direct-write varistor. Bi can be removed from these high-temperature varistors by two mechanisms: (1) substantial reaction at the ZnO film/alumina substrate interface and (2) Bi volatilization from the high surface area direct-write varistors.

Evidence of alumina–varistor surface interactions was observed for all direct-write varistors fired at 900°C and above. The interaction regions directly underneath the varistors are shown by SEM micrographs in Fig. 7 for the 900° and 1250°C direct write varistors. Reaction of the 900°C varistor with the alumina appears to be limited. Small pockets of Bi- and Si-rich second phases are observed at the three-grain intersections of the alumina substrate within 5 to 10 μm of the ZnO film/alumina substrate interface. Furthermore, there is a submicrometer interaction region at the very top of the alumina grains in contact with the varistor. The limited reaction of the varistor with the alumina substrate is a key reason that the 900°C varistor has superior electrical properties.

For the 1250°C varistor, shown in Fig. 7(b), the interaction region has increased in thickness by a factor of 10 to 20 times that of the 900°C varistor. Only Zn and Al are detected in this 5 to 10 μm layer. Unlike for the 900°C varistor, only a very few three-grain intersections of the alumina exhibit Bi- and Si-rich phases. A plausible explanation is that as the varistor is being heated, Bi-rich liquid phases interact preferentially with the small amount of Si-rich phase in the alumina. As temperatures increase above 900°C, substantial volatilization of Bi occurs, leaving both the varistor and the underlying interaction layer devoid of Bi.

The vigorous reaction of Bi and Si has precedence, as many glass frit containing electrodes are designed to wet ceramic

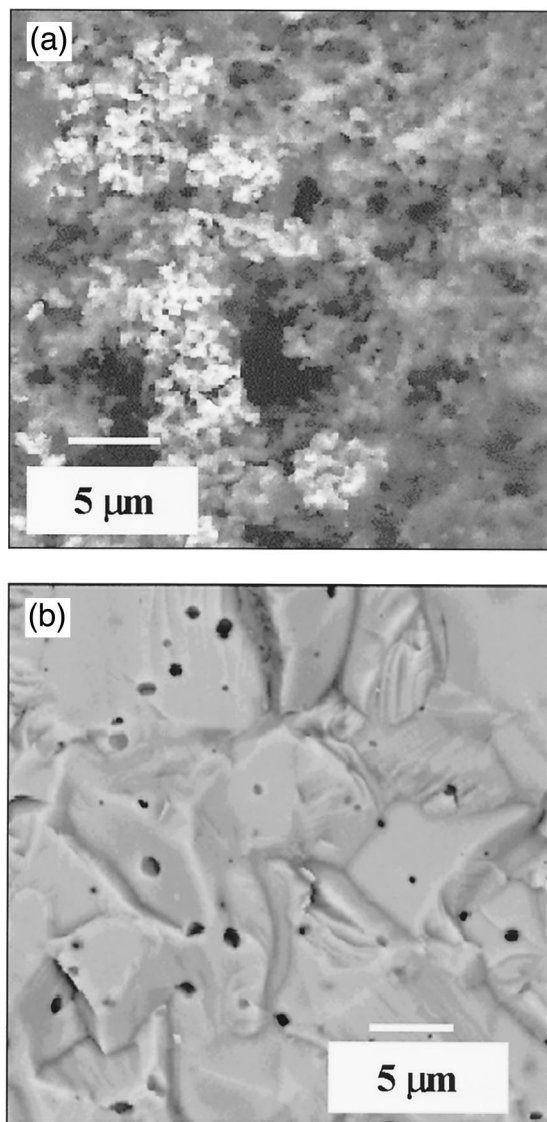


Fig. 6. Scanning electron micrographs of direct-write ZnO varistors patterned on dense alumina substrates sintered for 1 h at the following temperatures: (a) 800° and (b) 1250°C.

elements with Bi/Si compounds. As firing temperatures increase, Bi volatility increases greatly and removal of Bi from the active ZnO varistor region should increase substantially. Evidence for Bi volatilization comes from analysis of the reaction of Bi and Zn phases on the top surface of the alumina near the outside edges of the 900° and 1250°C varistors. For the 900°C varistor, this surface phase is bismuth-rich with a roughly 1:1 Bi:Zn ratio, as determined by EDS. For the 1250°C varistor, only Zn, no Bi, is observed on the top alumina surface near the edge of the varistor. Electrical measurements of the 1250°C varistor indicate completely ohmic behavior with resistivities comparable to those obtained for polycrystalline ZnO ceramics without additives. Thus, a reasonable mechanism for the decrease in α is that Bi is being vigorously removed from the varistor microstructure. To summarize, the direct-write ZnO varistor elements studied here have a narrow firing temperature range for acceptable electrical performance for two reasons: at low temperatures, the varistors do not densify to provide the necessary connectivity between Bi-rich grain boundaries, while at high temperatures, almost all Bi is removed from the varistor due to Bi volatility and preferential reaction with the underlying alumina substrate.

The relatively dense and uniform grain structure within the interior of the direct-write ZnO varistor heat-treated at 900°C is exhibited in Fig. 8. Equiaxed ZnO grains with a size range of

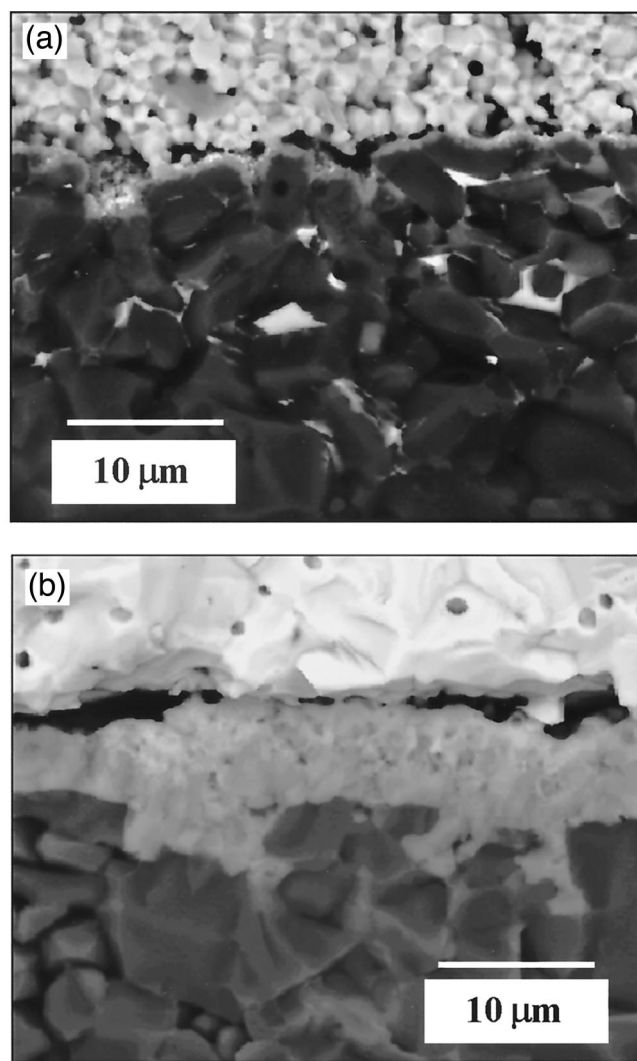


Fig. 7. Scanning electron micrographs of varistor–alumina substrate interaction underneath direct-write varistors fired at (a) 900° and (b) 1250°C, respectively.

roughly 1 to 3 μm are observed. Unlike the 800°C varistor microstructure, for which porosity accounted for greater than 30% of the volume, the apparent pore volume is on the order of 10%. The pores of the 900°C varistor are relatively uniform in size, being approximately 1 to 3 μm in dimension. Uniform grain size was observed from the top to the bottom of the 60 μm thick varistor film. Similar microstructures with limited loss of Bi are desired for a wider range of firing conditions. Appropriate diffusion barriers and capping layers will permit a wider firing temperature range for the fabrication of high nonlinearity coefficient, lower-field, direct-write varistors derived from the chemically prepared powders used in this study.

IV. Summary

ZnO varistor thick film pastes with tailored rheological behavior for direct-write fabrication of varistor elements have been developed. Paste formulations were optimized with respect to dispersant concentration, solids volume fraction, and vehicle composition. The pastes exhibited pseudoplastic rheological behavior with apparent viscosities of approximately 300 Pa·s in the deposition shear rate range, resulting in printed elements with relatively smooth surface topographies and uniform thickness (<5% deviation from average height). Aging phenomena were related to adsorption kinetics of the dispersant, which was accelerated at elevated temperatures. Varistor components prepared

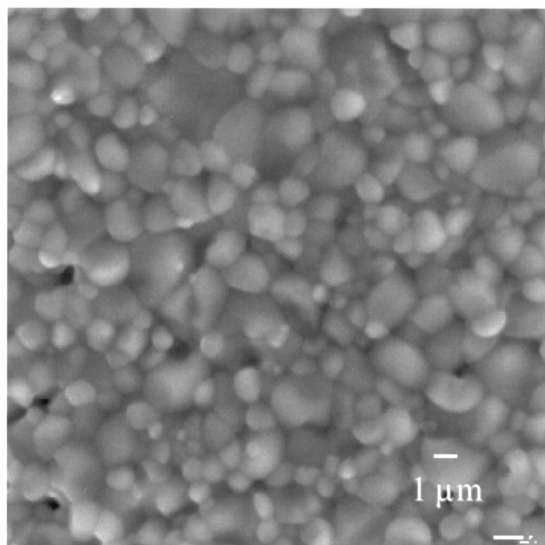


Fig. 8. Scanning electron micrograph of a direct-write ZnO varistor sintered on a dense alumina substrate at 900°C for 1 h.

from such pastes that were fired at 900°C for 1 h exhibited highly nonlinear current–voltage characteristics ($\alpha \sim 30$) in the breakdown regime. Reasonable structure–property relationships were developed that explained the narrow firing temperature range for acceptable electrical properties for microopen varistors. This work illustrates the generality of our approach for preparing functional ceramic inks for direct-write applications. By utilizing the processing guidelines established here and in our companion paper,²³ one can design suitable inks required for agile fabrication of multifunctional, multimaterial electroceramic devices.

Acknowledgments

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