

Sol-gel glass-coated zinc oxide for varistor applications

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ZnO varistors have excellent non-linearities and large surge-energy absorption capabilities. They have attracted much attention as transient-voltage absorbers and surge arrestors. Great achievements have been made in preparing high voltage ZnO varistors. With the development of modern electronic industries and communication technology, however, more and more low-voltage varistors are required for protecting equipment. In order to make low voltage components based on ZnO ceramics, two preparation processes are usually employed. (1) By adding a ZnO seed crystal, the grain size of ZnO ceramics is large enough to reduce the number of junctions between ZnO grains in a varistor. The seed crystal may be obtained by baking pure ZnO powders in NaOH/KOH melts [1] or at high temperatures ($> 1500^\circ\text{C}$) [2]. (2) Multilayer [3] or thin film [4] ZnO varistors have low breakdown voltages due to the smaller effective thickness.

This letter will present a novel method to prepare low-voltage ZnO varistors. Some initial results have been obtained.

In this study, ZnO powders were prepared by chemical precipitation and the B-Si-Pb coatings synthesized following a sol-gel process. The schematic plot of the varistor preparation is shown as Fig. 1. The starting composition of samples are listed in Table I.

After sintering, all samples were polished to remove a surface layer for a coating electrode. A Pd-Ag paste was printed on both sides of the

TABLE I Raw materials composition of varistors (unit: g)

	ZnO	Pb(Ac) ₂	B(OC ₄ H ₉) ₃	Si(OC ₂ H ₅) ₄	Glass (wt %)*
ZG01	4.95	0.043	0.052	0.012	1
ZG02	4.85	0.129	0.156	0.036	3
ZG03	4.75	0.214	0.260	0.059	5
ZG04	4.65	0.301	0.364	0.084	7
ZG05	4.75	/	0.260	0.059	5
ZG06	4.75	0.214	0.260	/	5
ZG07	4.75	0.214	/	0.059	5

* Proportion of components in glasses is $\text{B}_2\text{O}_3\text{:PbO:SiO}_2 = 2\text{:}2\text{:}1$ (mol).

sintered pellets and fired at 850°C for 15 min as an electrode for electrical measurements. The V – I characteristics of ZnO varistors were measured using an HP 4140B micro-current analyser. The breakdown voltage was defined as $V_{1\text{mA}}$.

Crystal phases of specimens were assessed by a Rigaku D/max-2400 type X-ray diffractometer. Microstructure profiles were recorded on an Amay scanning electron microscope.

The volume average particle size of pure ZnO powders precipitated is about 400–800 nm. Both precipitated powders and varistors coated by glasses show a single ZnO phase, which was identified by XRD patterns. Although the zinc borate phase with composition of $5\text{ZnO}\cdot 2\text{B}_2\text{O}_3$ could crystallize during cooling in a ZnO-glass system [5], no diffraction peaks of the compound in the materials appeared in this study, possibly because there is too little to detect.

Figs 2 and 3 depict the microstructure of some specimens sintered at different temperatures. For sample ZG03, the ZnO grain size gradually increases with increasing sintering temperature. The glass compositions apparently affect the ZnO grain size of specimens sintered at the same temperature. However, the change of ZnO grain size from 1000°C to 1100°C is larger than that from 1100°C to 1300°C . During sintering at an elevated temperature, the glass phase transformed into a liquid phase, making the sintering procedure rapid. The softening points of the B-Si-Pb glass are about 700 – 900°C , and the glasses become liquid phases with low viscosity at higher temperature. The viscosity of the glass increases with increasing temperature from 1000°C to 1100°C , and remains constant above 1100°C . Hence, the mechanism of ZnO grain growth at 1000°C to 1100°C is different from that at 1100°C to 1300°C , leading to the difference in grain growth rate [6].

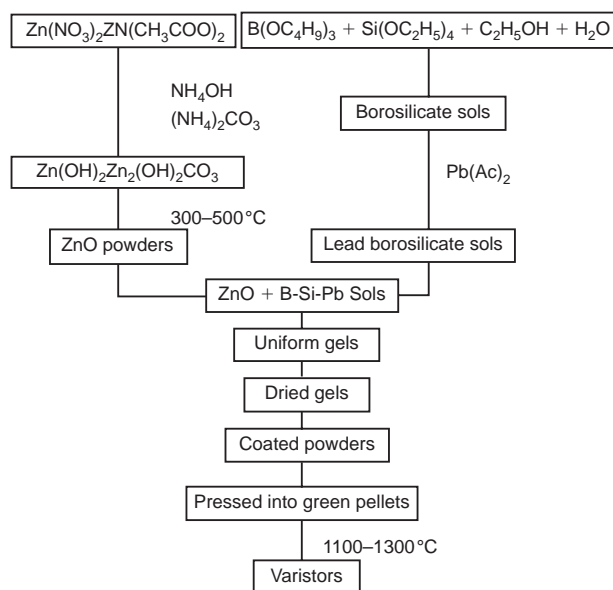


Figure 1 Preparation procedure of coated ZnO varistors.

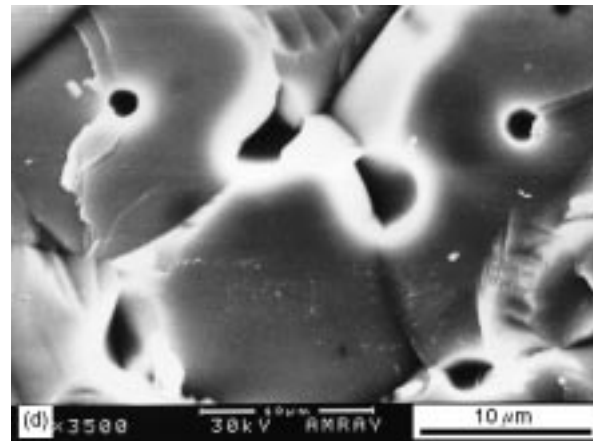
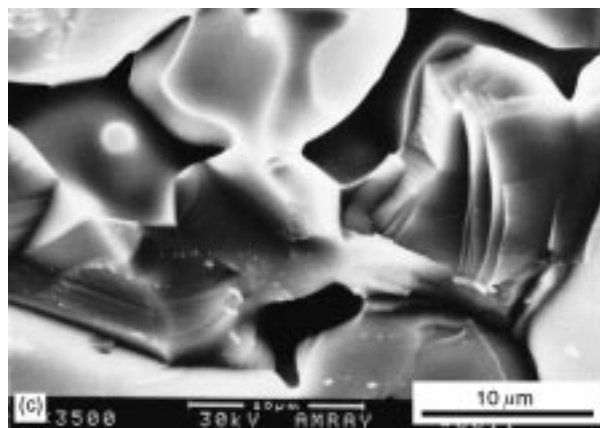
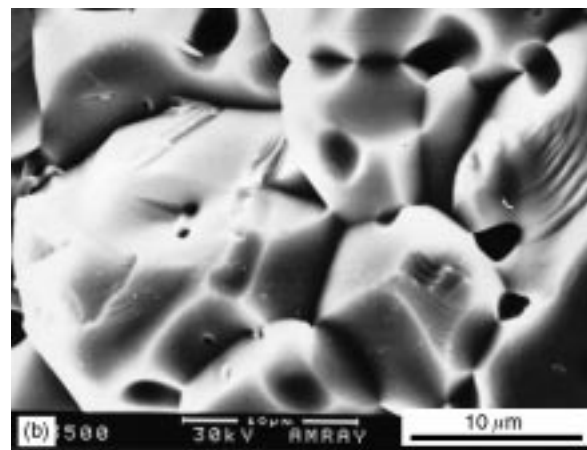
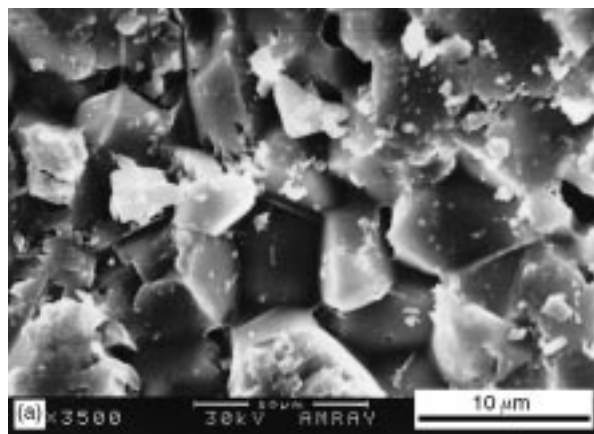


Figure 2 SEM profiles of sample ZG03 sintered for 1 h at (a) 1000 °C, (b) 1100 °C, (c) 1200 °C, (d) 1300 °C.

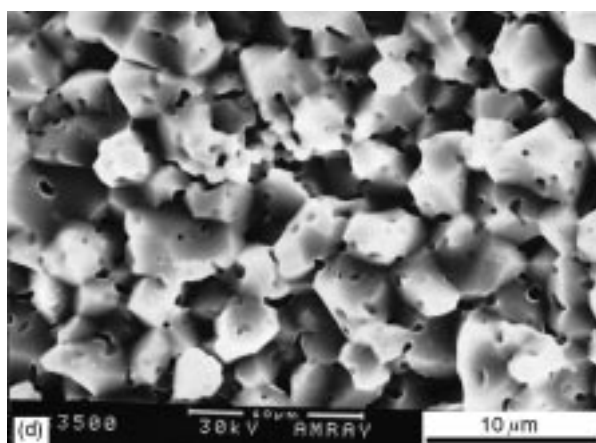
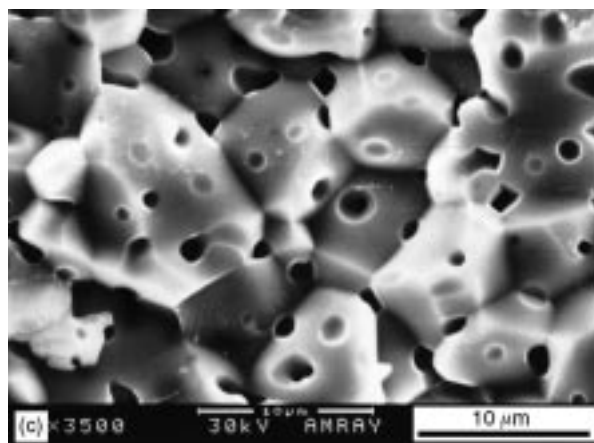
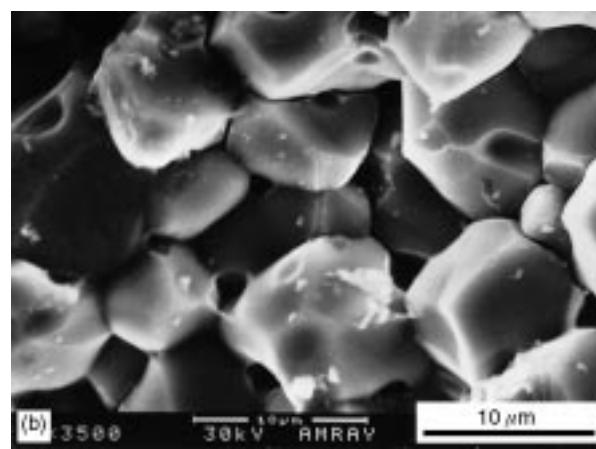
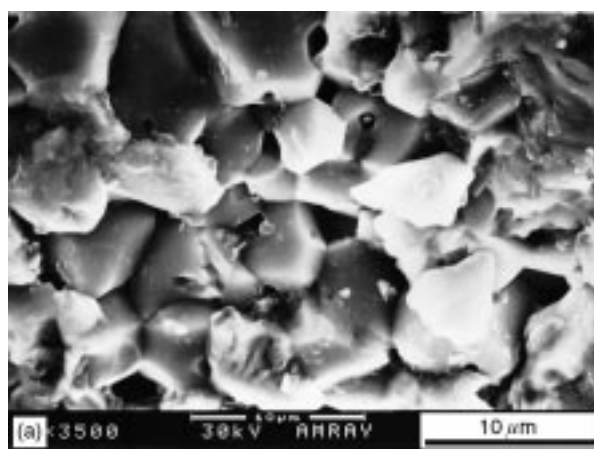


Figure 3 SEM photos of samples sintered at 1000 °C for 1 h at (a) ZG03, (b) ZG05, (c) ZG06, (d) ZG07.

TABLE II Summary of electrical properties (unit of V_{1mA} : $V \text{ mm}^{-1}$)*

	1100 °C			1200 °C			1300 °C		
	V_{1mA}	α	I_L (mA)	V_{1mA}	α	I_L (mA)	V_{1mA}	α	I_L (mA)
ZG01	2.8	1.87	/	0.64	1.62	/	0.81	2.0	/
ZG02	2.6	1.94	/	1.08	1.71	/	0.32	1.69	/
ZG03	45.2	5.15	/	9.75	2.70	/	2.33	1.79	/
ZG04	75.2	/	/	42.3	4.78	/	2.11	1.88	/
ZG05	0.61	1.78	/	0.31	1.75	/	/	/	/
ZG06	21.7	3.56	/	2.34	1.83	/	0.31	2.16	/
ZG07	/	/	/	2.05	1.74	/	0.25	1.98	/

*Leakage current I_L is defined as the current at the voltage of $0.8 V_{1mA}$.

Additionally, there are large amounts of pores in the ZnO grain and grain boundaries, especially for sample ZG06 and ZG07, which is probably due to combustion and volatility of organic compounds left in the materials.

The electrical properties of the varistors are summarized in Table II. The breakdown voltage (V_{1mA}) and nonlinear coefficient (α) of the samples sintered at the same temperature increase with increasing glass content. V_{1mA} values of the samples with the same composition decrease with increasing sintering temperature, while the reduction of α is not significant.

The breakdown voltage of a varistor is affected by the average grain size and the potential barrier height of the grain boundaries. The larger the grain and the lower the potential barrier height the lower the breakdown voltage [7]. In this work, the ZnO grain growth was enhanced by the B-Si-Pb glass liquid phases on one hand, and on the other hand, these liquid phases would crystallize at grain boundaries as the samples cooled from the sintering temperature to room temperature [5]. The phases crystallized from the glass formed a layer with higher resistivity at the grain boundaries of ZnO, which acted as a potential barrier in the varistors. The thickness of the crystal layer is in direct proportion to the glass content, so breakdown voltage of the varistors increased with increasing glass content. That the varistors sintered at higher temperature had lower non-linear coefficient might be attributed to the evaporation of the glass, resulting in reduction of the crystal layer thickness. For all varistors, the leakage current is very high, which is

necessarily reduced by modifying the preparation procedure or adjusting the composition of the glass. This work is now underway in our laboratory.

The main conclusions from this work are:

(1) Sol-gel-coated ZnO varistors with low breakdown voltage have been prepared by chemical precipitation and sol-gel technology.

(2) Breakdown voltage and non-linear coefficient of the samples sintered at the same temperature increase with increasing glass content. V_{1mA} values of the samples which are based on the same composition decrease with increasing sintering temperature, while the change of α is not significant.

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