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Analysis of ZnO varistors prepared by the sol–gel method

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Abstract

A new sol–gel processing method to prepare ZnO-based varistor powders, using inexpensive zinc acetate dihydrate, ethylene glycol, *n*-propyl alcohol and glycerol as starting materials, is presented. Compared to conventional oxide-mixing techniques, this method yields powders with a more homogeneous distribution of dopants; the sintering temperature could be lowered by about 200 K to 1000°C and the grain size is much smaller which proves very helpful for achieving high breakdown strength. Microstructure and electrical characteristics of the sintered powders were investigated.

Keywords: A. Sintering; A. Sol–gel processes; B. Grain size; D. ZnO; E. Varistors

1. Introduction

ZnO powders are very important materials due to many interesting properties inherent in this material, such as dielectric [1], piezoelectric [2], pyroelectric [3], semiconducting [4], acousto-optic [5], optical [6], electro-optical [7], nonlinear optical [8], photoelectrochemical [9] and electrical properties [4]. Moreover, ZnO ceramics containing several metal oxides, such as Cr_2O_3 Bi_2O_3, Sb_2O_3, Co_3O_4, MnO_2 etc., show highly nonlinear current-voltage characteristics which enables them to be used as protection devices against voltage surges and voltage transients [10–15]. The varistor effects take place at the grain boundaries within the ceramics and numerous theories have been developed to explain the effect [16–18]. It is necessary to have homogeneous distribution of dopants and the correct oxygen concentration to form good varistor ceramics, since oxygen defects are presumed to be the reason for ZnO-conductivity. Commercial varistor powders are usually produced utilizing a conventional mixed oxide technique with ZnO and other metal oxide dopants as starting materials, which is recognized as being unsuitable for achieving homogeneous dopant distribution. Many papers have been published about new methods to prepare varistor powders [19–23]. A sol–gel method has been shown to achieve high breakdown fields by small grain size [24].

In this paper, we use a different way to process sol–gel powder for varistor application by using inexpensive source materials such as zinc acetate dihydrate, ethylene glycol, *n*-propyl alcohol and glycerol. The powders can be sintered at a lower temperature compared to the conventional mixed oxide method and provide smaller grain size than has been published elsewhere. Moreover, microstructure and electrical characteristics of the sintered powders were investigated.

2. Experimental procedures

2.1. Preparation of powders

The sol was prepared using zinc acetate dihydrate, ethylene glycol, *n*-propyl alcohol, and glycerol. Twenty five milliters of ethylene glycol was added to 100 g of zinc acetate dihydrate in a round bottomed flask fitted with a condenser and kept at 150°C for 15 min over a hot plate to obtain a uniform transparent solution. On cooling to room temperature the content of the flask solidified to a transparent brittle solid which could be dissolved in *n*-propanol 200 ml. The solution thus obtained was highly water sensitive and readily gelled on addition of a few drops of water. Triethylamine (1 mol equivalent) was also added to help hydrolysis of the

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zinc acetate. The resulting solution was colorless and transparent. The solution was then slowly heated to about 500 and 700°C for 5 h to remove all organics. The pure ZnO powders were obtained, plastified and granulated with 1 wt% PVA. The procedure of the powder preparation is shown in Fig. 1.

ZnO-based ceramics containing several metal oxides were then prepared using the same preparation method mentioned above. The dopant composition in the final oxide powders is ZnO: 96.99 mol%; Sb_2O_3: 1.0 mol%; Bi_2O_3, Co_3O_4, MnO_2, Cr_2O_3: each 0.5 mol%; B_2O_3: 0.25 mol%; Al_2O_3: 0.01 mol%, according to Ref. [24]. The pure ZnO and ZnO-based powders were then sintered at 900–1200°C for 2 h. The phase relations for the sintered bodies were identified using a Rigaku Rint X-ray diffractmeter (XRD). The microstructures were observed using scanning electron microscope (HITACHI Model S-4200 Field Emission SEM), and bulk density, ρ (g/cm^3) was determined by Archimedes method. The average grain size of ZnO ceramics was determined by dividing the length of a line by the number of grain boundaries intercepting it.

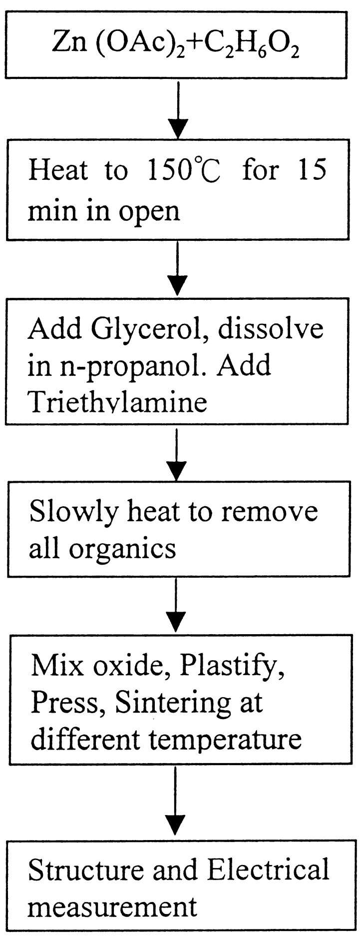


Fig. 1. Flow diagram for the sol–gel preparation method.

2.2. Measurement of electrical properties

The voltage-current characteristics of the ZnO varistors are expressed by $I = CV^{\alpha}$ where V is the voltage across the sample and I is the current flowing the sample. The non-ohmic coefficient was found from

$$\alpha = \mathrm{dlog}(I)/\mathrm{dlog}(V)$$

I–V characteristics of the samples were measured by using sine wave high-voltage supply in the current range up to 50 mA.

3. Results and discussion

Table 1 shows the density, electrical resistance and grain size of pure ZnO powders sintered at different temperatures (termed as sample S1). The highest density is obtained about 5.4 g/cm^3 which is more than 95% of the theoretical density as the sintering temperature is 1050°C (refer to Fig. 2). The maximum value of the electrical resistance is found to be about 156 MΩ as the

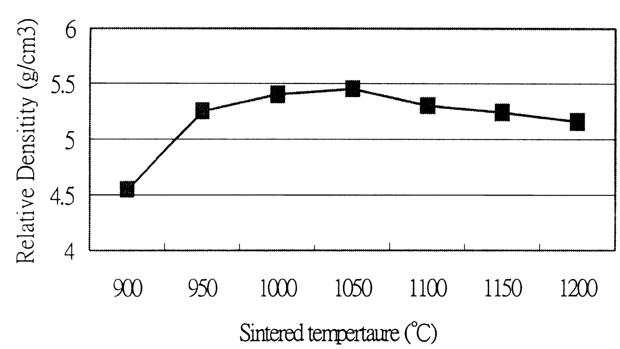


Fig. 2. The dependence of relative density on the sintering temperature of pure ZnO samples S1.

Table 1
Results of measurements of pure ZnO samples sintered at different temperature

Sintering temperature	900°C	950°C	1000°C	1050°C	1100°C	1150°C	1200°C
Density g/cm^3	4.55	5.25	5.40	5.45	5.30	5.24	5.16
Resistance (max) MΩ	16	24	156	148	144	142	72
Grain Size μm	0.26	0.31	0.38	0.56	0.85	0.97	1.42

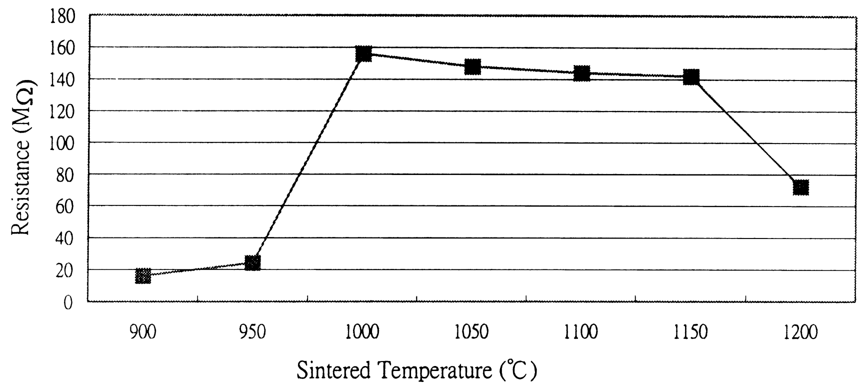


Fig. 3. The dependence of resistance on the sintering temperature of pure ZnO samples.

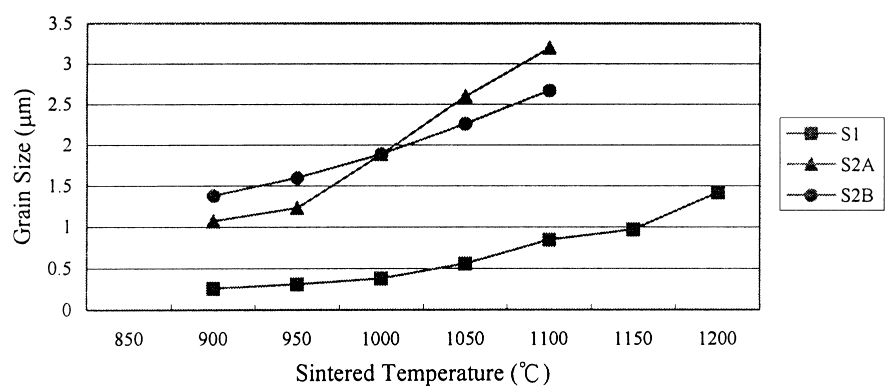
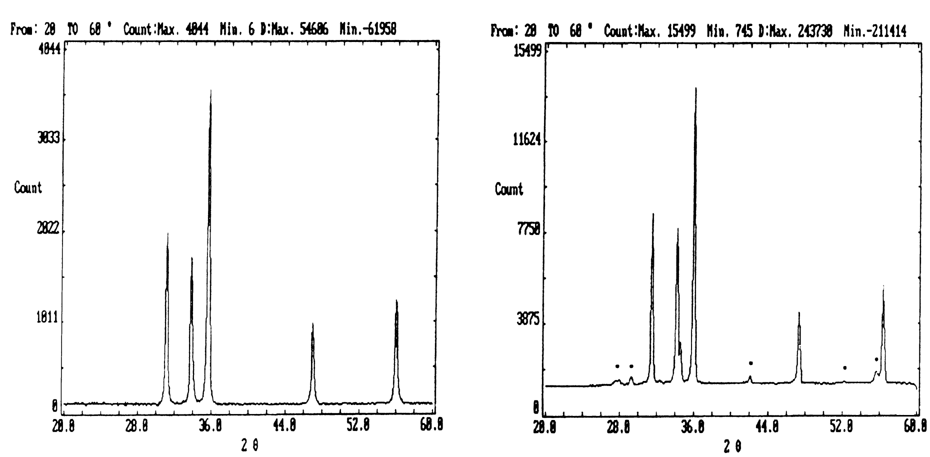


Fig. 4. The dependence of grain size on the sintering temperature of pure ZnO samples S1 and ZnO-based samples heated at 500°C S2A and 700°C S2B.

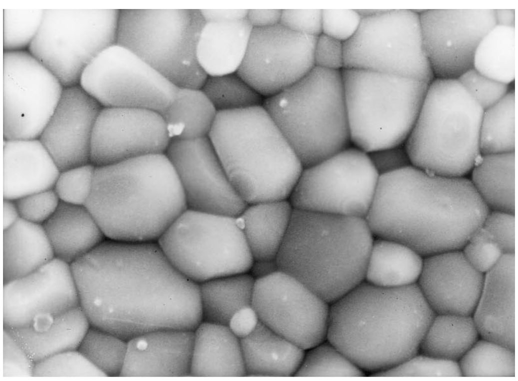


(a) pure ZnO S1 (b) ZnO-based S2A

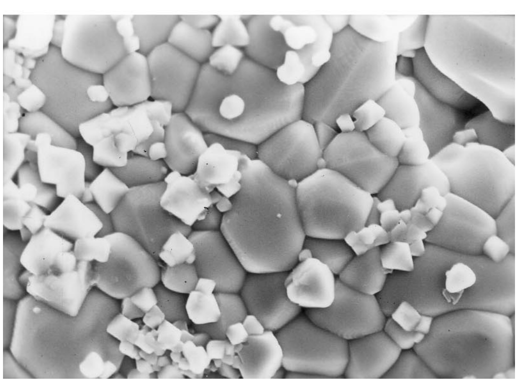
Fig. 5. X-ray diffraction pattern of (a) pure ZnO and (b) ZnO-based ceramics sintered at 1100°C.

sintering temperature is 1000°C (refer to Fig. 3). The electrical resistance of the sample could not be too small, or the sample would break down even if a small voltage applied. The grain size increases with increasing sintering temperature (refer to Fig. 4). The average grain size increases with increasing sintering temperature as well as the sintering time and can be explained according to the phenomenological kinetic grain growth equation expressed as [25]:

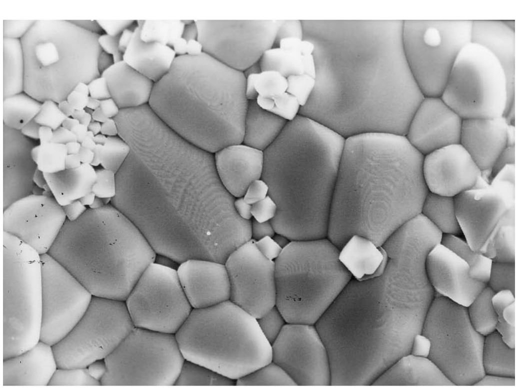
$$\mathrm{Log}G = (1/n)\log t + (1/n)[\log K_0 - 0.434(Q/RT)]$$



(a)



(b)



(c)

Fig. 6. SEM microstructure of sol–gel prepared powders sintered at 1100°C.

Where G is the average grain size at the time, the n value is the kinetic grain growth exponent, K_0 is a constant, Q is the apparent activation energy, R is the gas constant, and T is the absolute temperature. The grain size of ZnO-based samples (termed as S2) with a calcining temperature of 500°C (termed as S2A) and 700°C (termed as S2B) for 5 h and sintered at 900–1100°C are also shown in Fig. 4. Compared to S1 and S2, the grain size of the S2 sample is larger than that of S1, which is in agreement with other published papers [24]. The grain size of S2A sample is smaller than that of S2B sample sintered at a lower temperature (900 and 950°C); coincides at 1000°C, and the grain size of S2A sample is larger than that of the S2B sample sintered at a higher temperature. Fig. 5 shows the typical X-ray diffraction patterns of the pure ZnO and ZnO-based ceramics sintered at 1100°C for 2 h. Comparing Fig. 5a with 5b, an additional peak is caused by the doping. Fig. 6 shows the microstructure examined by SEM of S1 (Fig. 6a) and S2 (Fig. 6b and c) sintered at 1100°C for 2 h. The grain size for S1 is about 0.4 μm and that for S2 is about 1.7 μm. The grain size for conventional ZnO varistors is larger than 2 μm. ZnO varistors with small grain size could lead to a significant reduction in the overall size of the device for a given voltage and to high-voltage applications. Therefore, the break down strength of our sample is expected to be much higher compared to conventional varistors. The current-voltage characteristics of the S2 varistors sintered at different temperatures are shown in Fig. 7. The calculated α value is about 40–60. Threshold voltage is important electrical parameter that is necessary for quantitative evaluation of the rated varistor voltage. Fig. 8 displays the dependence of sintering temperature on the threshold voltages of S2A and S2B samples. The threshold voltage increases as

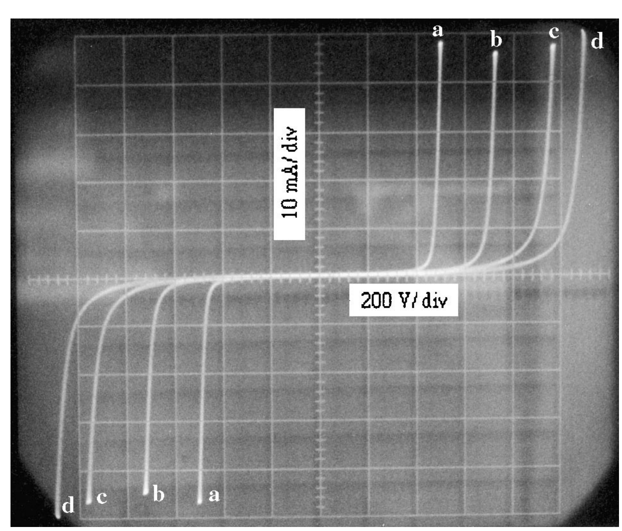


Fig. 7. Current-voltage characteristics of ZnO varistors with different sintering temperature.

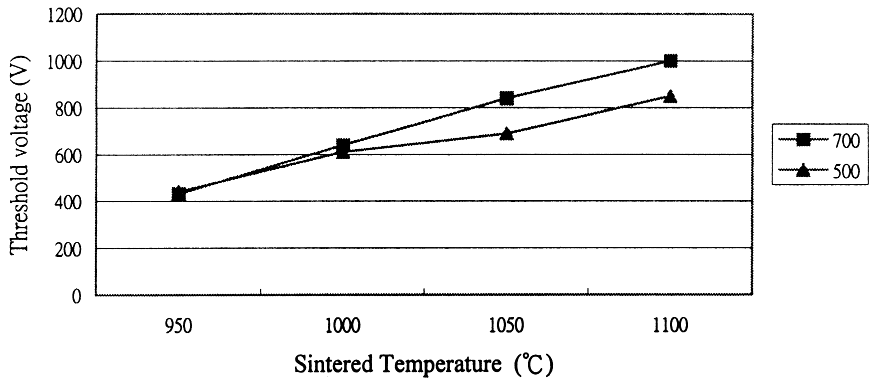


Fig. 8. The dependence of threshold voltage on the sintering temperature of ZnO-based varistors.

the sintering temperature increases and S2B samples have a larger threshold voltage. Thus, the desired threshold voltage can be obtained by changing the sintering temperature.

4. Conclusions

Homogeneous pure ZnO and ZnO-based powders prepared by the sol–gel method have been successfully fabricated. Compared to conventional oxide-mixing techniques, the sintering temperature could be lowered by about 200 K to 1000°C and the grain size is much smaller (< 2 μm) which is expected to show superior electrical properties.

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