J Electroceram (2008) 21:528–531
DOI 10.1007/s10832-007-9234-z

Study on the ZnO-based ceramic films for low-voltage varistors with high stability

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Published online: 1 September 2007

Abstract ZnO-based ceramic films for low-voltage varistors were fabricated by a novel sol-gel process. The stability of ZnO-based ceramic films has been studied by improving the degradation properties and increasing the microstructure compactness of the films. The degradation of the film varistors was improved via doping with Na^+ and heat-treating in oxygen ambient. The microstructure compactness was increased via eliminating the microspores and improving uniformity of the grain size of ZnO by doping with B_2O_3. The results indicated that ZnO-based ceramic films for low-voltage varistors with high stability can be obtained while the concentration of doped Na^+ is 20–40 ppm, B_2O_3 is 0.25–0.5 mol.% and being heat-treated in oxygen ambient for 2 h.

Keywords ZnO · Varistors · Stability · B_2O_3

1 Introduction

ZnO-based varistors are characterized by highly nonlinear current-voltage characteristics and a high energy absorption capability [1]. As a result they are widely used as surge absorbers in electronic circuits, devices and electrical power systems to protect against dangerous over-voltage surges [2, 3]. ZnO-based ceramic films have great potentials and advantages of fabricating low-power low voltage varistors [4].

In practice, ZnO varistors are always subjected to a continuous normal electrical stress, lightning surge, and switching surge. Under such surges, they are gradually degraded with time [5–7]. Therefore the high electrical stability is very important in the light of reliability of various electrical and electronic systems.

In this paper, ZnO films were deposited on Au/Si substrates by a novel sol-gel process. The stability of ZnO-based ceramic films has been studied by improving the degradation properties and increasing the microstructure compactness of the films. The aging property was improved by acceptor doping and heat-treating in oxygen. And the electric properties were improved by increasing the microstructure compactness of the film varistors.

2 Experimental procedures

ZnO ceramic films were deposited on Au/Si substrates by a novel sol-gel process. The sols were prepared by zinc acetate dihydrate [Zn $(CH_3COO)_2{\cdot}2H_2O$; 99.9%, chemical purity], dopants, such as Bi $(NO_3)_3{\cdot}5H_2O$, Mn $(CH_3COO)_2{\cdot}4H_2O$, Co $(NO_3)_2{\cdot}6H_2O$, Cr $(NO_3)_3{\cdot}9H_2O$, Sb_2O_3 and the solvents, such as 2-methoxyethanol. ZnO-based ceramic films were prepared on the substrates by repeated spin coating at room temperature. In order to improve the degradation properties of the film varistors, ZnO-based ceramic films were doped with Na^+ and sintered in oxygen ambient, respectively. To increase the microstructure compactness of the film varistors, ZnO films were doped with B_2O_3.The phases of the samples were analyzed with Japanese RIGAKU D/max-3B X-ray diffractometer(XRD) with $Cu\,K_\alpha$ radiation (30 kV, 30 mA).The leakage currents(I_L) were surveyed with MY-4C varistors synthesize parameter testing instrument and the microstructure was studied via scanning electron microscopy (SEM).

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3 Results and discussion

3.1 Study of degradation properties

Figure 1 is the leakage current of variety Na^+ doped ZnO-based ceramic films at 115°C. It has shown that the aging property of the film was improved remarkably. It is because alkali metal ions such as Li^+, Na^+, K^+ take up the places of interstitial Zinc ions in ZnO crystal. So they restrain interstitial Zinc ions' formation and impede their transfer. Thus acceptor doping can reduce the content of interstitial Zinc ions and increase the stability of the film [8–10]. But when the quantity of the doped Na^+ reached 80ppm, the initial leakage current of the doped ZnO film increased distinctly. It was declared that doped with 20–40 ppm Na^+ whose radius is close to Zn^{2+} was most suitable to improve the aging property.

Figure 2 shows the leakage currents of ZnO-based ceramic films before and after heat-treating in oxygen ambient for 2 h. It was seen that the aging property of the ZnO film was improved and the change extent along with time was reduced after heat-treating in oxygen ambient. The results may due to the different partial pressures of oxygen between oxygen and air. The high partial pressure of oxygen makes oxygen diffuse rapidly in ZnO grain boundary and promotes the combination of oxygen and interstitial Zinc ions in ZnO crystal and then reduces the density of interstitial Zinc ions [11, 12]. It is also propitious to the formation of rich oxygen layer. Thus heat-treating in oxygen ambient was found to improve the aging property too.

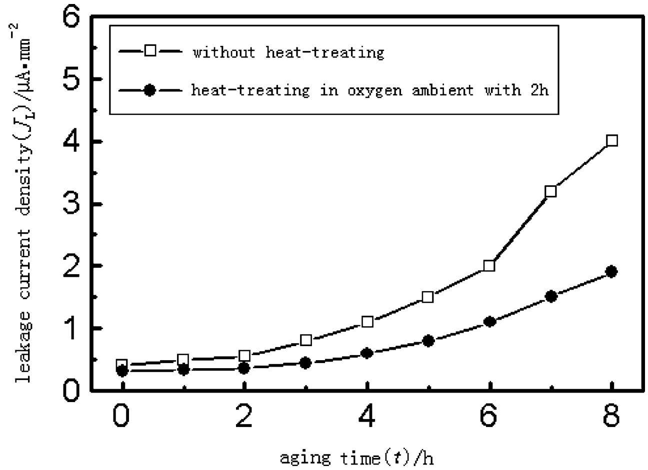

Fig. 2 The leakage current of the films before and after heat-treating in oxygen ambient

3.2 Study of microstructure compactness

The ZnO-based ceramic films were fabricated by a novel sol-gel process in which ZnO nano power was dispersed in the precursor, so it was easy to produce microspores. The annealing process could eliminate the microspores in certain extent but not completely. Figure 3 shows the SEM micrographs of ZnO-based ceramic film with microspores. These microspores turn to incipient fault of invalidating ZnO-based ceramic films for low-voltage varistors. Therefore, eliminating microspores and increasing the microstructure compactness of the films are important for improving the stability of ZnO-based ceramic films. Figure 4 shows the SEM micrographs of ZnO films doped with 0.25 and 0.5 mol.% B_2O_3, respectively. Compared with the film in Fig. 3, the compactness of the ZnO films was improved evidently. The film doped with 0.25 mol.% B_2O_3 was smoother and the microspores decreased greatly. While the quantity of B_2O_3 reach 0.5 mol.%, the compactness of the film was improved distinctly and the microspores were rare. It indicates that B_2O_3 has a good effect on eliminating microspores.

B_2O_3's effect on compacting ZnO films is derived from its low melting point. B_2O_3 begins to melt gradually and

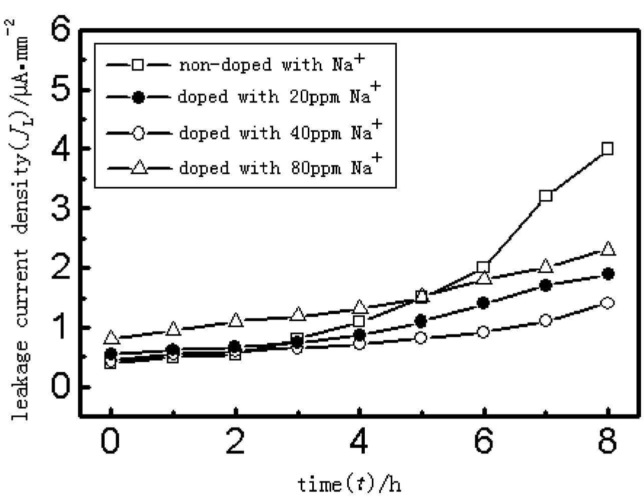

Fig. 1 The leakage current of ZnO film with variety doped Na^+

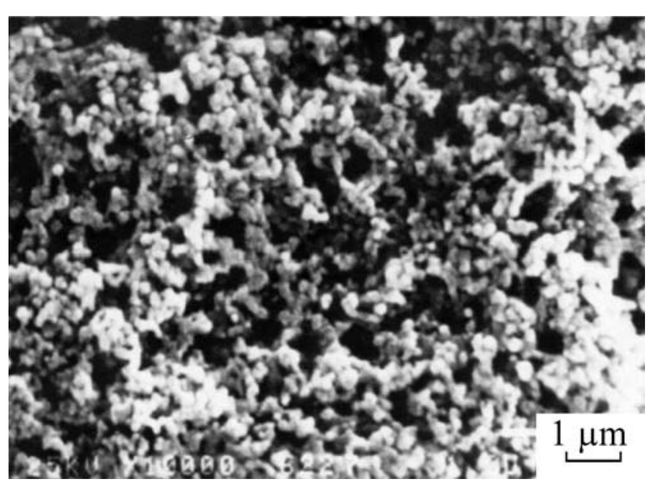

Fig. 3 SEM micrographs of film with microspores

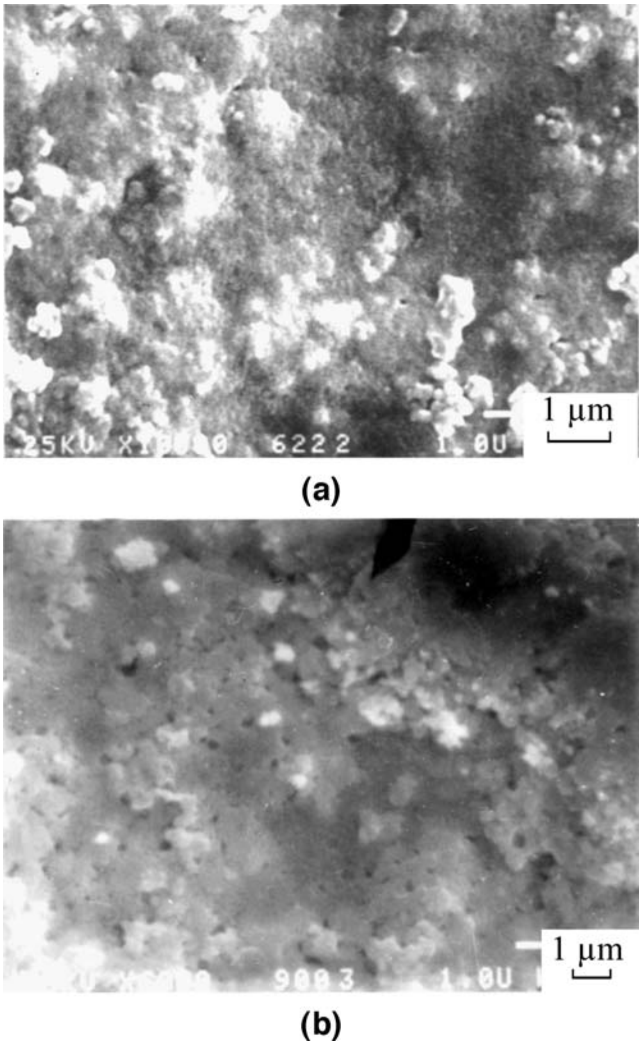

Fig. 4 SEM micrographs of ZnO films with (**a**) 0.25 mol.% B_2O_3 and (**b**) 0.5 mol.% B_2O_3

forms liquid phase at 500 °C, that has a good effect on the redistribution of separate composition and the growth of crystal grain. Meanwhile it supplies a condition to the movement of ZnO grains and the elimination of micro-spores. While the temperature goes on rising, doped Bi_2O_3 begins to melt. Not only the existence of two liquid phases adds to the amount of liquid phases, but also their difference at melting point remarkably widens the temperature range of films' liquid phase annealing. The compatible of the two liquid phases effectively avoids distributing uniformity of the component [13–15]. Figure 5 shows X-ray diffraction pattern of ZnO films doped with 0.25, 0.5, 0.75, 1.0 mol.% B_2O_3, respectively. It could be seen that most diffraction peaks were equal. The growth character of crystal phase and para-crystal phase were not influenced with the additional B_2O_3. We conclude that the XRD patterns of films are not immune to the amount of B_2O_3.

Figure 6 shows the results of electrical properties of ZnO films with different B_2O_3 additive. When the doped B_2O_3

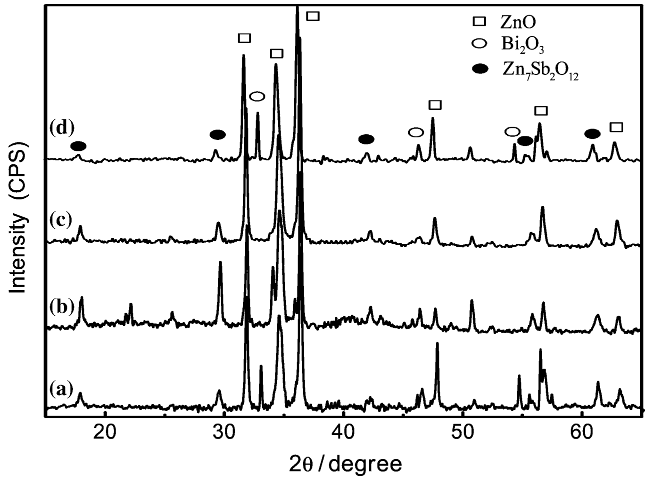

Fig. 5 X-ray diffraction patterns of ZnO films doped with (**a**) 0.25 mol.%, (**b**) 0.5 mol.%, (**c**) 0.75 mol.%, (**d**) 1.0 mol.% B_2O_3

was 0.25–0.5 mol.%, the nonlinear coefficient reduced slightly but the leakage current of the sample decreased and the stability improved notability. So the optimal doped B_2O_3 quantity is 0.25~0.5mol.%.

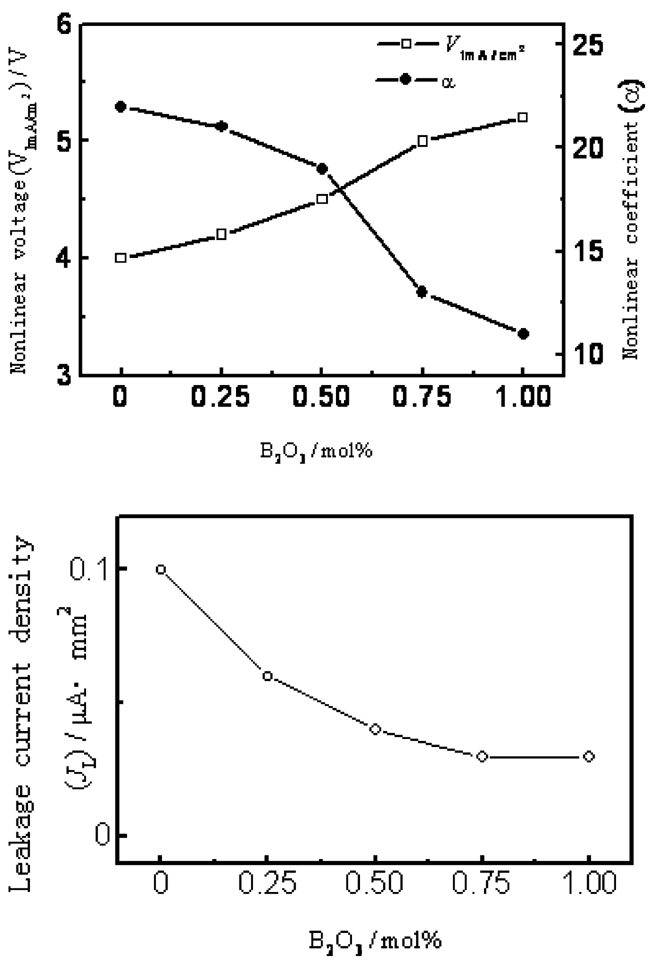

Fig. 6 Electrical properties of ZnO films with different B_2O_3 additive

4 Conclusions

ZnO-based ceramic films for low-voltage varistors were fabricated by a novel sol-gel process. The stability of ZnO-based ceramic films has been studied. The results indicate that ZnO-based ceramic films for low-voltage varistors with high stability can be obtained when the concentration of Na^+ is 20–40 ppm, B_2O_3 is 0.25–0.5 mol.% and being heat-treated in oxygen ambient for 2 h.

Acknowledgements This study was supported by the Major State Basic Research Development Program of China (973 Program), No.2004CB619300 and the program for new century excellent talents in university (NCET-04-0703).

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