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Short Communication

Nonohmic properties of V/Mn/Nb/Gd co-doped zinc oxide semiconducting varistors with low-temperature sintering process

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ABSTRACT

The microstructure and nonohmic properties of the $ZnO–V_2O_5–MnO_2–Nb_2O_5–Gd_2O_3$ (ZVMNG) semiconducting varistors were systematically investigated at low sintering temperature. With increasing sintering temperature, the average grain size increased from 4.1 to 11.7 μm, the sintered densities decreased from 5.54 to 5.42 g/cm^3, and the breakdown field decreased noticeably from 7138 to 920 V/cm. The sample sintered at 900 °C exhibited excellent nonohmic properties, which are 66.1 in the nonohmic coefficient and 77 μA/cm^2 in the leakage current density.

1. Introduction

Advanced electronic devices such as OLED TV, smart phone, digital camera, tablet PC, notebook, etc. consist of semiconductor devices in core functional components. The development of semiconductor industry will enable electronic devices to have new functions and high speed as well as upgraded functions. However, the semiconductor devices are more susceptible to transient overvoltages such as switching of electrical loads, magnetic and inductive coupling, electrostatic discharge (ESD), and so on. The majority of electronic components such as diodes, transistors (power), ICs, and passive components will be damaged at less than 10 mJ. Today, electronic systems are very complex and denser, because of a number of components and extremely narrow space between electric lines. Thus electronic systems are more vulnerable to transient overvoltages.

ZnO semiconducting varistors are electroceramic devices made by sintering ZnO powder doped with various minor additives, such as Bi_2O_3 (or Pr_6O_{11}), CoO, Cr_2O_3, etc. [1,2]. They exhibit symmetric *V–I* characteristics similar to those of a back-to-back Zener diode [1,2]. For this reason, ZnO semiconducting varistors are extensively used to protect electronic systems and electrical power systems from transient overvoltages [1,2].

Commercial multilayered chip varistors are based on $ZnO–Bi_2O_3$ semiconducting ceramics and $ZnO–Pr_6O_{11}$ semiconducting ceramics. They have to use an expensive refractory Pd or Pt as an inner-electrode because they have a desirable ceramic sinterability at a relatively high temperature above 1000 °C. $ZnO–V_2O_5$ semiconducting ceramics have an important advantage, which can use pure Ag having the highest conductivity as an internal electrode [3,4]. $ZnO–V_2O_5$-based semiconducting ceramics are being studied as only multilayered chip varistors, unlike Bi_2O_3- and Pr_6O_{11}-doped ZnO semiconducting ceramics [5–15]. In the light of researched results until now, V_2O_5-doped ZnO semiconducting varistors should be studied in many points. The specific additives and sintering process are important ceramic variables, which can improve nonohmic properties in the $ZnO–V_2O_5$-based semiconducting varistors [5–13]. Therefore, it is very interesting to investigate the effects of sintering process on nonohmic properties for the varistor ceramics with specified composition. In this work, effect on microstructure

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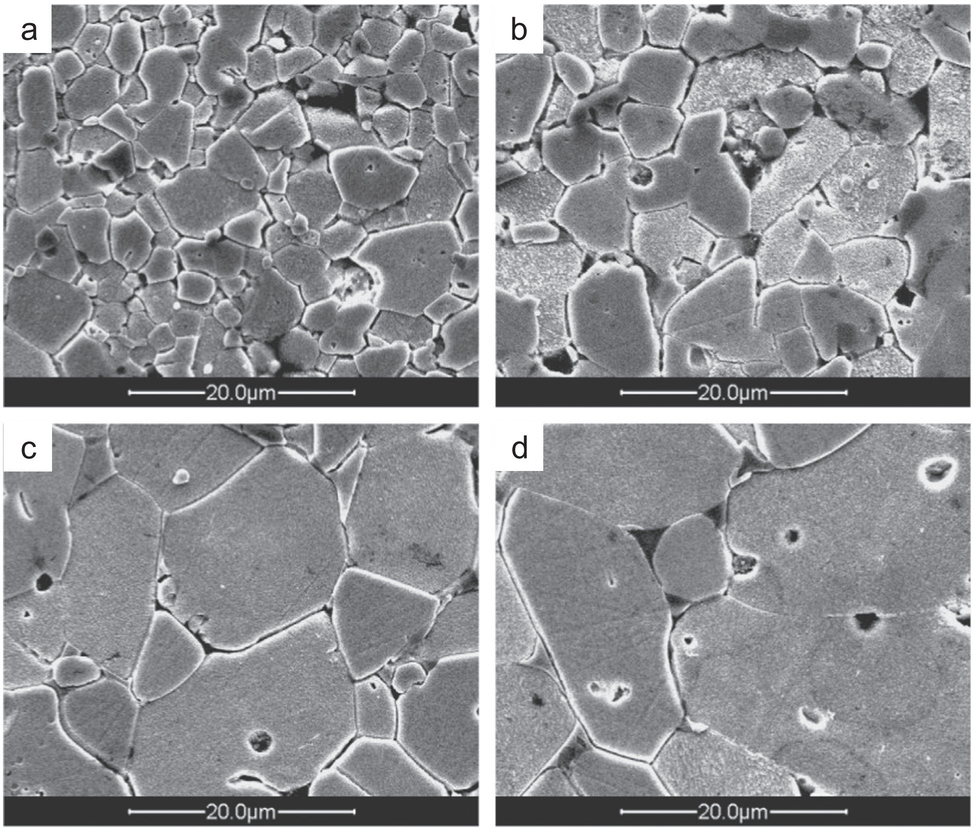

Fig. 1. SEM micrographs of the samples for different sintering temperatures: (a) 875 °C, (b) 900 °C, (c) 925 °C, and (d) 950 °C.

and nonohmic properties of the $ZnO–V_2O_5–MnO_2–Nb_2O_5–Gd_2O_3$ (ZVMNG) semiconducting varistors was investigated by sintering at a low-temperature, and a surprising high nonohmic coefficient was attained using proper sintering temperature.

2. Experimental procedure

The varistor raw materials were prepared in the proportion of $97.35ZnO+0.5V_2O_5+2.0NO_2+0.1Nb_2O_5+0.05Gd_2O_3$ (all in mol%). Raw materials were mixed by ball milling with zirconia balls and acetone in a polypropylene bottle for 24 h. The mixed slurry was dried at 120 °C for 12 h. The dried mixture was mixed by a magnetic stir bar into a beaker with acetone and 0.8 wt% polyvinyl butyral binder of powder weight. After drying, the mixture was granulated by sieving through a 100-mesh screen to produce the starting powder. The sieved powder was pressed into disk-shaped pellets 10 mm in diameter and 1.5 mm in thickness at a pressure of 100 MPa. The pellets were set on a MgO plate into an alumina sagger and sintered at four temperatures (875 °C, 900 °C, 925 °C, and 950 °C) in air for 3 h, and furnace-cooled to room temperature. The heating and cooling rates were 4 °C/min. The final pellets were about 8 mm in diameter and 1.0 mm in thickness. Conductive silver paste was coated by screen-printing techniques on both faces of the pellets and the electrodes were formed by heating it at 550 °C for 10 min. The electrodes were 5 mm in diameter. Finally, after the lead wire was soldered to both electrodes, the samples were packaged by dipping them into a thermoplastic resin powder.

Both surfaces of the sintered pellets were lapped and ground with SiC paper and polished with 0.3 μm-Al_2O_3 powders to a mirror-like surface. The polished pellets were chemically etched into $1HClO_4$:$1000H_2O$ for 25 s at 25 °C. The surface microstructure was examined using a field emission scanning electron microscope (FESEM, Quanta 200, FEI, Brno, Czech). The average grain size (d) was determined by the linear intercept method [16]. The crystalline phases were identified using an X-ray diffractometer (XRD, X′pert-PRO MPD, Panalytical, Almelo, the Netherlands) with Ni-filtered CuK_α radiation. The densities (ρ) of sintered pellets were measured using a density determination kit (238490) attached to a balance (AG 245, Mettler Toledo International Inc., Greifensee, Switzerland).

The electric field–current density (E–J) characteristics were measured using a V–I source (Keithley 237, Keithley Instruments Inc., Cleveland, OH, USA). The breakdown field (E_B) was measured at a current density of 1.0 mA/cm^2 and the leakage current density (J_L) was measured at 0.80 E_B. The nonohmic coefficient (α) was calculated from $\alpha=(\log J_2-\log J_1)/(\log E_2-\log E_1)$, where E_1 and E_2 are the electric fields corresponding to $J_1=1.0$ mA/cm^2 and $J_2=10$ mA/cm^2, respectively. Three samples (with the same sintering temperature) were used for all electrical measurements and the average value was obtained.