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Effect of V_2O_5 on electrical and microstructural properties of ZnO ceramics

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ABSTRACT

ZnO ceramics with small amounts of V_2O_5 as a varistor-former ranging from 1–5 mol% were prepared by conventional powder processing route and sintered at 700, 800 and 900 °C for 2 h. It was observed that the grain growth behavior in ZnO ceramics was strongly influenced by doping with V_2O_5. Morever, lower temperatures about 900 °C could be used for sintering. The microstructure of the samples consists of ZnO grains as a main phase and $Zn_3(VO_4)_2$ as a secondary phase. All of the prepared ceramics showed characteristic of non-ohmic current–voltage behavior. Non-linear coefficient increased with increase in V_2O_5 content and sintering temperature. Activation energy of the ceramics lies in the range of 0.071–0.402 eV which decreased with increase in V_2O_5 content and sintering temperature. The origin of the non-linear electrical behavior was explained by considering the solid state reactions and formation of the potential barriers at grain boundaries.

1. Introduction

Zinc oxide based varistor is a typical sort of semiconductor ceramics. Varistors are electronic devices with nonlinear current–voltage characteristics which are employed in voltage surge protection applications. The combination of high nonlinearity and high-energy absorption capability coupled with low power loss has made the ZnO varistor extremely attractive for high power applications [1–3].

The ZnO-based varistor consists predominantly of ZnO, with small additions of Bi_2O_3, Sb_2O_3, CoO, MnO, Al_2O_3 and other constituents such as Cr_2O_3.The nonlinear current–voltage characteristic of these materials is a grain-boundary phenomenon and directly related to the size of the grains. Thus, practical applications are required to test the potential barriers between the grains in the presence of these additives. Accordingly, the method of preparation, crystalline size, and homogeneity of the additive are critical for producing good varistor materials [4,5]. In fact, it is necessary to have homogeneous distribution of dopant and the correct oxygen concentration to form good varistor ceramics.

The non-linearity of the varistors can be described in terms of a non-linear coefficient α which is defined by $I=KV^{\alpha}$, where I is the current, V the electric potential and K a constant of proportionality [1].

The binary ZnO–V_2O_5 system has been studied mostly in glassy material. However, the electrical properties in the ceramic state of these binary oxides are interesting. It was found that, other than heavy elements, the relatively light element vanadium is also another possible candidate that can act as a new varistor-forming ingredient for the fabrication of ZnO varistors. Moreover, these ceramics can be sintered at relatively low temperature, i.e. about 900 °C. This is important for applications in which it can be a multi-layered chip component, because it can be co-fired with a silver inner-electrode (m.p. 961 °C) without using the expensive palladium or platinum metals [6–8].

In this work, the effect of V_2O_5 concentration (1, 2, 3, 4 and 5 mol%) as a varistor-former on the microstructure and electrical properties of ZnO ceramics were investigated at different sintering temperatures; 700, 800 and 900 °C. Furthermore, the mechanism of potential barrier formation and its relationship to the chemical of grain-boundary are discussed and clarified.

2. Material and methods

Samples were prepared by the conventional ceramic fabrication procedure. The reagent grade Vanadate pentoxide ranging from 1–5 mol% was mixed with zinc oxide powder by ball-milling with zirconia balls for 6 h. After milling, the obtained powder was pressed into disks of 10 mm in diameter and 1 mm in thickness without binder. The disks were sintered at 700, 800 and 900 °C in air for 2 h and cooled to room temperature. The sintered samples were covered by silver paste for electrical measurements. Density of samples was measured at room temperature using the Archimedes method. The phase analysis of the samples was carried out by X-ray diffractometry (XRD; PW1710, Philips) using Cu Kα radiation. The microstructure of the sintered specimens was examined using a scanning electron microscope (SEM; Cam Scan

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MV2300). Finally, the current–voltage behavior was measured using variable D.C. power supply and an electrometer (Model 617, Keithley, USA) in direct current mode.

3. Results and discussion

In the prepared ceramics, the presence of the vanadium intergranular phase was proved by SEM images and X-Ray diffraction pattern. Figs. 1–3 show SEM micrograph of the samples, sintered at different temperatures. They showed large grains with oblong shape dispersed in a matrix composed of small grains. It can be seen that the grain size increases with increase in sintering temperature. Also the addition of V_2O_5 has the tendency to promote grain growth of ZnO. The high reactivity of the V-rich liquid phase during sintering caused such a grain growth. V-rich liquid phase accelerated the solution and precipitation process of grains, and effectively helped the grains to move easily. As a result, small grains near V-rich grain boundaries dissolved more easily than big grains. The dissolved grains moved through the liquid phase and precipitated in the surface of big grains with low surface energy, then the big grains became bigger and bigger. At last, the exaggerated grains formed [9].

Fig.4 depicts XRD patterns of prepared ceramics. Pronounced diffraction peaks of hexagonal ZnO are observable at $2\theta=31.8^{\circ}$, 34.5°, 36.3°, 47.7° and 56.7°. In addition, peaks of $Zn_3(VO_4)_2$ secondary phase were found at $2\theta=20.9$, 26.8, 29.2, 30.1,33.8 and 51.5 [10,8]. In fact, the grain growth with increasing of V_2O_5 content can be related to the formation of $Zn_3(VO_4)_2$ phase, which acts as a liquid-phase sintering aid at high temperature [7].

Fig.5 shows densification behavior of specimens, in which density of ZnO ceramic increased with increase in V_2O_5 content. High density sample was obtained for sintering temperature of 900 °C with 5 mol% V_2O_5.

Zinc oxide shows n-type behavior due to the oxygen vacancies [11]. However, it was found that the addition of V_2O_5 in zinc oxide made the electrical conduction behavior non-ohmic [8]. The current–voltage characteristic of ZnO–V_2O_5 varistors is very sensitive to ceramic microstructure, due to abnormal grain growth of ZnO grains in presence of V_2O_5. Two important factors effect the non-linear property of this binary system; Sintering temperature and V_2O_5 content.

Fig.6 shows electric field versus current density (*E–J*) curve of the samples at room temperature. It can be seen that the conduction characteristics are divided into two regions, which are of high resistance (ohmic region) and very low resistance (non-ohmic region). In the non-ohmic region the current increased much more quickly than the voltage; the sharper the knee of the curves between the two regions, the better the nonlinear properties. It is clear that, in the prepared ceramics, the knee gradually became pronounced in accordance with increase in V_2O_5 content. In other word, with increase in V_2O_5 content, the non-linear property increased. Also the onset electric field (the point at which non-linearity begins) decreased with increase in V_2O_5 content.

The non-linear coefficient value (α) was obtained by linear regression of the logarithm scale plot of current density versus applied electrical field. Fig.6 shows variation of α in terms of V_2O_5 content, sintered at different temperatures in which α value increased with increase in V_2O_5 content and sintering temperature. Obtained results have been summarized in Table 1. The sample with 5 mol% V_2O_5 sintered at 900 °C exhibits the highest nonlinearity coefficient. It should be mentioned that the α values, obtained in this work, is below that of Bi_2O_3-doped multicomponent ZnO varistors. However, we can get to this result

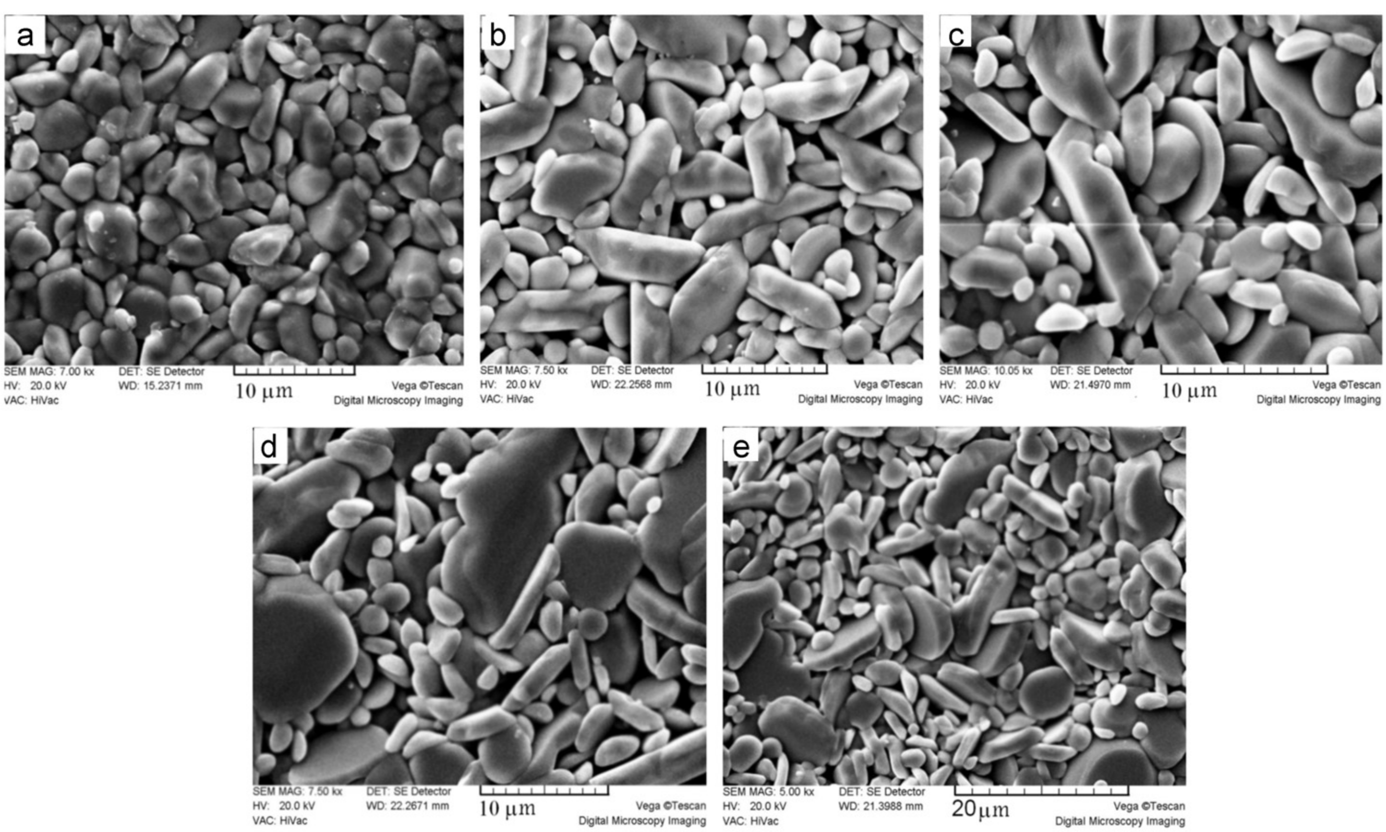

Fig. 1. SEM micrographs of ceramics sintered at 900 °C containing various amounts of V_2O_5: (a) 1 mol%, (b) 2 mol%, (c) 3 mol%, (d) 4 mol%, and (e) 5 mol%.