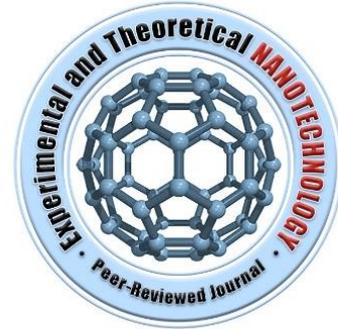


Study of non-ohmic electrical behavior and microstructure of ZnO-V₂O₅ varistor



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Electronic ceramics based on ZnO with 1,2,3,4 and 5 mol% of V₂O₅ were prepared by conventional powder processing route and sintered at 1000 °C for 2 hour. Microstructure of samples was investigated by X-Ray and SEM. It was observed that the microstructure of the samples consists of ZnO grains as main phase, and the density of samples was increased with increase in V₂O₅ content. All of the prepared ceramics showed characteristic of non-ohmic current – voltage behavior. Non-linear coefficient increased with increase in V₂O₅ content. The non-linear electrical behavior was explained by considering formation of the potential barriers at grain boundaries.

Keywords: Varistor; ZnO grain; Break down voltage.

1. INTRODUCTION

Today, electronic equipment contains small and fast semiconductor devices, which could be damaged by low transient voltage surges and therefore by reducing transient voltage surges, most high voltage substations and distribution equipment can be made less costly and more reliable. Varistors are available to protect circuits over a very wide range of voltages, from a few volts for low-voltage varistors in semiconductor circuits to tens of kilovolts for electrical power distribution networks [1-3]. 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 [4].

Matsuoka et al. [5] in the early 1970s reported that polycrystalline ZnO ceramics incorporated with several transition metal oxides showed a highly non-ohmic conduction. Since then, many researches and studies have been performed on the fabrication and the physicochemical properties of this material. Zinc Oxide is an n-type semiconductor with direct band gap and multi-junction grain boundary with an electrostatic potential barrier between grains in the sintered body, compared with back-to-back Zener diode using single pn-junction for Si. This possesses a much higher energy handling capability than the Zener diode. Non-linear current–

voltage characteristic of ZnO varistors are directly related to their microstructure, specifically the ZnO grain size that affects the varistor breakdown voltage. To achieve a given breakdown voltage, one can change either the varistor thickness or the grain size. Also the method of sintering process is critical for producing good varistor materials [6-7]. The advantage of vanadium-doped ZnO varistors is that the ceramic can be sintered at a relatively low temperature of about 900 °C. This is important for multilayer components because such ceramics can be co-fired with a silver inner-electrode having a melting point of around 960°C. V₂O₅ is also a better sintering aid compared to Bi₂O₃ since it has been found that V₂O₅-doped ZnO materials can be densified to the same density at a lower temperature compared to Bi₂O₃-doped ZnO materials [8,9].

In this work, the effect of V₂O₅ concentration (1, 2, 3, 4 and 5 mol%) on the microstructure (grain size and shape) and electrical properties (breakdown point and non-linear coefficient) of ZnO ceramics were investigated. Furthermore, the mechanism of potential barrier formation between grain-boundary are discussed and clarified.

2. EXPERIMENTAL PROCEDURE

Samples according to general formula; ZnO_{(100-x)%}-V₂O_{5(x)%} where x=1,2,3,4,5 mol% were prepared by the conventional ceramic fabrication route. Vanadate pentoxide was mixed in proper ratios according to the formula with Zinc Oxide powder by ball-milling with zirconia balls for 4 h. After milling, the obtained powder was pressed into disks of about 12mm in diameter and 1mm in thickness without binder. The disks were sintered at 1000 °C in air for 2 h and cooled to room temperature. Electrodes formed by silver paste onto the sample surfaces, were used for the electrical measurements. Phase analysis of the samples was carried out by X-ray diffractometry (XRD; PW1710, Philips) using Cu K α radiation. The microstructures of the sintered specimens were examined using a scanning electron microscope (SEM, Cam scan MV2300). Electrical current-voltage behaviour was measured with an electrometer (Model 617, Keithley, USA) and in direct current mode.

3. RESULTS AND DISCUSSION

It is widely observed that the change of dopant concentration always indicates significant influence in the properties and performance of the electronic ceramics products. In the prepared electro-ceramics, SEM images and X-Ray diffraction pattern proved the presence of the vanadium intergranular phase. Figs. 1 show SEM micrograph of the samples. They showed large grains with oblong shape dispersed in a matrix composed of small grains. It was found that, grain size increases with increase in V₂O₅ content. In other word, addition of V₂O₅ 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 diffuse 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, where the big grains grow bigger and bigger. Finally, the exaggerated grains formed [10].

Density of the samples was measured at room temperature using the Archimedes method. It was found that density lie in the range of 5.2-6.3 gr/cm³ which increase with increase in V₂O₅

content. In order to examine whether any additional phases are formed during sintering process, we carried out the structural investigation using the X-ray powder diffraction technique. Powder XRD pattern of the sample with 5 mol% of V_2O_5 is given in Fig. 2. X-Ray pattern of other samples were similar to this figure. According to references, pronounced diffraction peaks of hexagonal ZnO are observable which has been shown with Z. In addition, peaks of $Zn_3(VO_4)_2$ secondary phase were found [11,9,16].

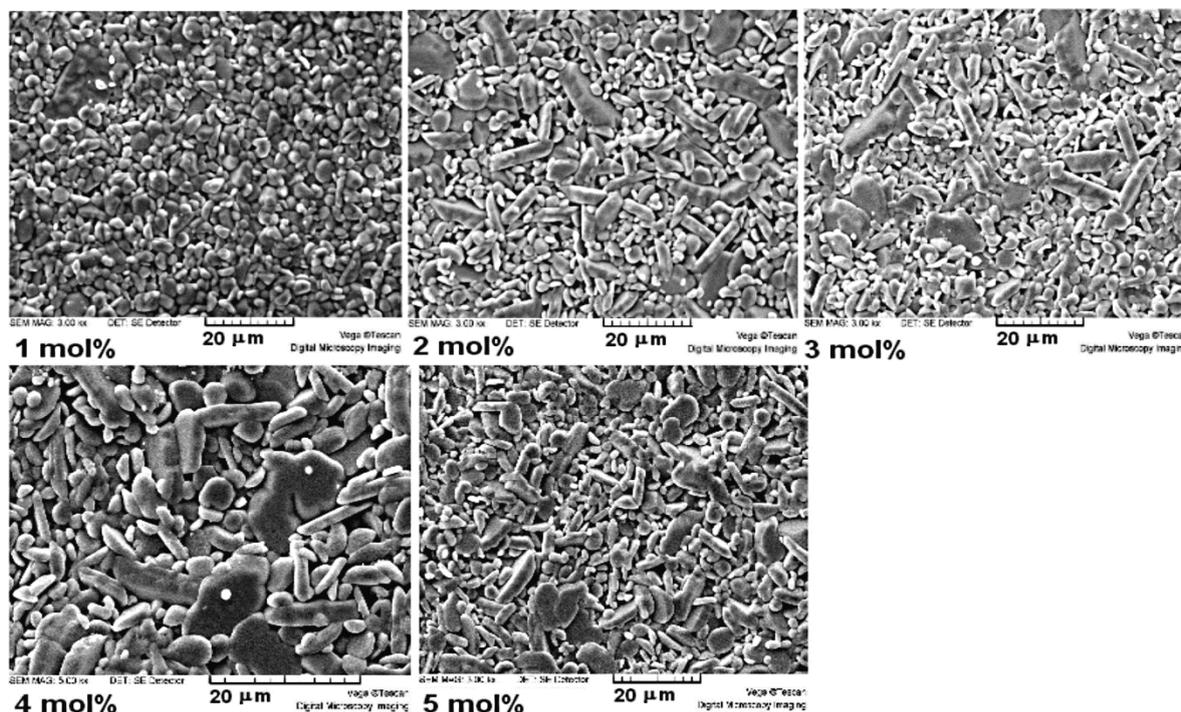


Figure 1 SEM micrograph of the samples.

I-V characteristic (current-voltage) of Zinc oxide varistors with V_2O_5 dopant is very sensitive to the microstructure due to abnormal grain growth of ZnO grains in the presence of V_2O_5 . Fig.3 shows I-V characteristic of the samples at room temperature. It is clearly shown that the conduction is non-ohmic and the curves are divided into ohmic regions, which are of high resistance and very low resistance or non-ohmic region. In the non-ohmic region the current increases much more quickly than the voltage. It is clear that, in the prepared ceramics, the knee gradually becomes more pronounced in accordance with increasing V_2O_5 content. In other word, with the increase in V_2O_5 content, the non-linear property increases. Also, breakdown point (the point at which non-linearity begins) decreases with increasing of V_2O_5 content. The non-linear coefficient values (α) were obtained by linear regression of the logarithm scale plot of current density versus applied electrical field; $\alpha = d(\log I)/d(\log V)$ [12]. The value of α lies in the range of 3.79-5.4 . It was found that, α value increases with increase in V_2O_5 content and the sample with 5 mol% V_2O_5 exhibits the highest nonlinearity coefficient. It should be mentioned that, in the V_2O_5 -doped system, much lower temperature can be used for sintering. Electrical characteristic of the prepared samples has been summarized in Tab 1.

The non-linear property of the varistors is explained by the existence of potential barrier at the grain boundaries [13]. In practice, there are a variety of inter-grain conduction paths that operate in parallel in varistors. These can be through the grain boundary region or through the bulk inter-granular material. In fact transition metal oxides, are involved in the formation of interfacial states and deep bulk traps at grain boundaries, providing large potential barriers to give better nonlinear characteristics [14]. This barrier is Schottky-type in which conduction in linear region dominated by thermionic emission over this Schottky barrier. Also, the conduction in non-linear region is dominated by Follower–Nordheim field emission through the Schottky barrier [13].

Table 1 Electrical properties of the samples.

| Sample | ZnO (mol%) | V ₂ O ₅ (mol%) | Density (gr/cm ³) | Non-linear coefficient (α) | Break down Voltage (Volt) |
|--------|------------|--------------------------------------|-------------------------------|-------------------------------------|---------------------------|
| C1 | 99 | 1 | 5.2 | 3.79 | 15.6 |
| C2 | 98 | 2 | 5.39 | 3.95 | 13.5 |
| C3 | 97 | 3 | 5.8 | 4.5 | 13 |
| C4 | 96 | 4 | 6.05 | 5.22 | 12.2 |
| C5 | 95 | 5 | 6.3 | 5.4 | 10.8 |

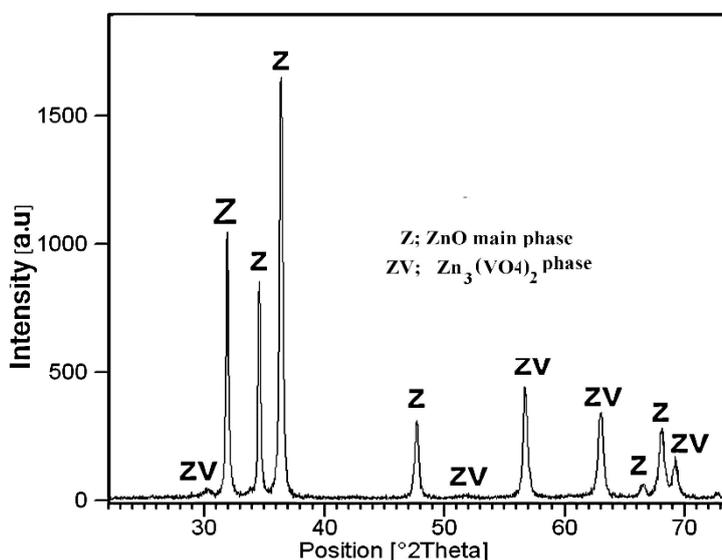


Figure 2 X-Ray diffraction pattern of C5.

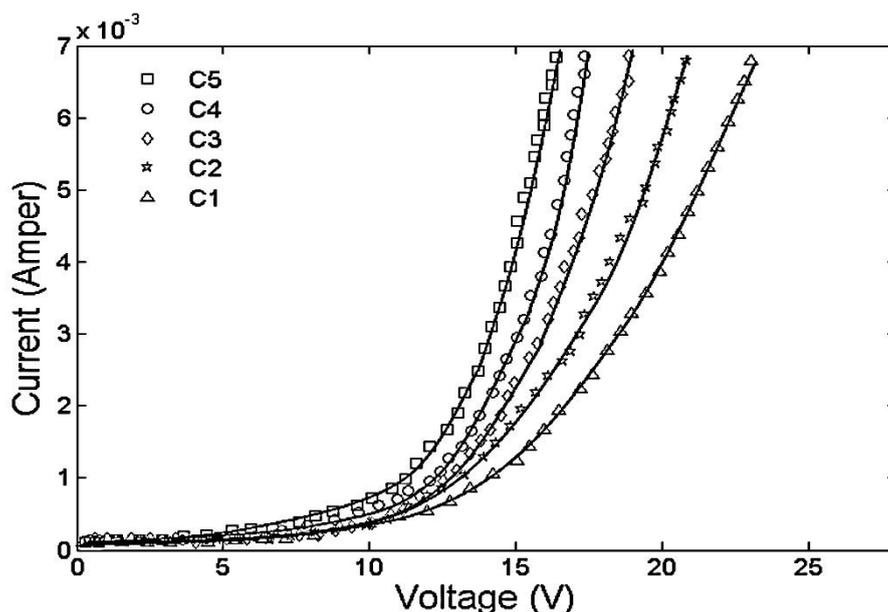


Figure 3 I-V characteristic of the samples.

In other words, the I-V characteristic of the electro-ceramic is controlled by the existence of potential barrier at the grain boundaries. The grain-boundary is treated as a junction in which the Fermi level of the bulk or grains are different from that of the layer between two grains. When the junction is formed and equilibrium is reached, the Fermi level is the same along the junction so that the binding energy gained by an electron occupying a trap state is equal to the electrostatic energy spent in moving an electron from the interior of the grains to the boundary. The result of this equilibrium is that the interface trapped electrons act as a sheet of negative charge at the boundary, leaving behind a layer of positively charged donor sites on either side of boundary, and creating an electrostatic field with a barrier at the boundary [5]. Thus, we can attribute this behavior (increase in nonlinear coefficient with increase in V_2O_5 content) to a lowering of the grain boundary barrier height [15].

4. CONCLUSIONS

The effect of small amount of V_2O_5 (1-5 mol%) content on the microstructure and electrical properties of the ZnO ceramic were investigated. The grain growth of ZnO are strongly influenced by doping with V_2O_5 . It was found that ZnO doped with V_2O_5 resulted in a vanadium-rich intergranular phase formed between the ZnO grains. The abnormal grain growth of ZnO grains was observed in the presence of V_2O_5 in which the grains size increase with increasing of V_2O_5 content. Similarly the non-linear coefficient increased with increasing of V_2O_5 content. The non-linear electrical behavior is inferred to be due to the existence of potential barrier at the grain boundaries.

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