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STUDY OF THE EFFECT OF WO_3 AND Bi_2O_3 ON THE MICROSTRUCTURE AND ELECTRICAL PROPERTIES OF A TiO_2 BASED VARISTOR

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ABSTRACT

Titanium dioxide (TiO_2) varistors doped with tungsten oxide (WO_3) and bismuth oxide (Bi_2O_3) were investigated. The microstructure and electrical characterization were studied, where the effects of different concentrations of WO_3 and a fixed amount of Bi_2O_3 were investigated. TiO_2 based varistors have promising potential for the high performance development. The percentage of dopant was varied at various levels and the prepared samples were then characterized by evaluating IV relationships to determine the degree of non-linearity in the varistor. Evaluation was conducted based on non-linear coefficients, breakdown voltage and power loss. Microstructure analysis was also carried out using SEM. The average grain size was determined to find the relationship between microstructure and electrical properties. It was found that a molar concentration with 99.1%TiO_2. 0.4%WO_3. 0.5%Bi_2O_3 yielded the best results in terms of electrical and microstructural properties. The addition of 0.5%Bi_2O_3 and 0.4%WO_3 creates a relatively low clamping efficiency, higher non-linear coefficient, low breakdown voltage and less power loss.

Keywords: TiO_2 varistor powder; Tungsten Oxide (WO_3); Bismuth Oxide (Bi_2O_3), electrical properties; microstructure analysis.

INTRODUCTION

Varistors are electroceramic devices with non-linear current and voltage characteristics which act as surge protectors against transient voltages in electrical and electronic equipment. The current voltage relationship, which is also known as the power law, is expressed as $I=KV^{\alpha}$, where α is the non-linear coefficient. Breakdown voltage is defined as the greatest reverse voltage that can be applied without exponential increase. A varistor in the pre-breakdown region follows Ohm's law, where current increases with the increase of voltage. In the non-linear region, it acts as a transient voltage suppressor where it is able to react when there is a momentary overload voltage. It clamps current to prevent it increasing when the voltage is increasing. When the current does not increase, the device or equipment is therefore protected. In the upturn region, when voltage increases, current also increases. At low voltage, it acts as an insulator where resistance is high and at high voltage, it acts as a conductor where the resistance is low (Bueno, Varela, Barrado, Longo, & Leite, 2005). Today, smaller integrated circuits are more and more in demand, and so there is a need to create low voltage varistors which have high linear coefficients and low breakdown voltage.

TiO_2 is a versatile material which has garnered much attention (Chen, Zou, Wang, & Zhang, 2010) and which has unique characteristics that have been used in various fields (Ali, Mustapa, Ghazali, Sujitno, & Ridha, 2013; Aznilinda, Herman, Ramly, Raudah, & Rusop, 2013; Mahendran, Lee, Sharma, & Shahrani, 2012; Navale, Vadivel Murugan, & Ravi, 2007; Singh & Singh, 2011). TiO_2 has been used in fields such as those involving cosmetics, pigments and capacitors (Thamaphat, Limsuwan, & Ngotawornchai, 2008). Researchers have found that TiO_2 varistor materials can be used to meet the demands for today's modern electronic devices since it has been observed that its behavior is suitable for low voltage applications (Sousa, Oliveira, Orlandi, & Longo, 2010). The most common varistor materials used in the industry today are SiC and ZnO (Pianaro, Bueno, Longo, & Varela, 1995). ZnO varistors display a high non-linear coefficient but are not suitable for low voltage applications since they have low permittivity (Li et al., 2003; Mohammadi Aref, Bidadi, & Hasanli, 2010). As for SiC varistor materials, it has lower non-linear coefficient compared to ZnO materials (Li et al., 2001). TiO_2 varistor materials were first investigated by Yan and Rhodes (1981) with the addition of (Nb, Ba) and a non-linear coefficient of 3-4 was achieved (Yan & Rhodes, 1981). Many researchers have observed that low breakdown voltage and a reasonably high non-linear coefficient can be obtained with TiO_2 varistor materials. The effect of Tantalum Pentoxide (Ta_2O_5) on TiO_2 varistors was investigated in (Navale et al., 2007), where it was observed that Ta_2O_5 was able to improve the non-linear coefficient.

The addition of WO_3 was investigated by Su et al. (2003) and it was found that a high non-linear coefficient could be obtained. WO_3's high density also improves the strength of the material. The addition of Bi_2O_3 improves the densification and grain growth kinetics (Yongvanich, Jivaganont, Sakasuphalerk, Huayhongthong, & Suwanteerangkul, 2010). WO_3 high density also increases electrical conductivity (Wang et al., 2012). The addition of Bi_2O_3 improves the sintering process of the material, and it has good non-linear electrical properties (Yaya & Dodoo-Arhin, 2012). Investigations have found that the oxides tend to segregate the boundaries (Bomio, Sousa, Leite, Varela, & Longo, 2004). In this work, WO_3 and Bi_2O_3 were added to improve the microstructure and electrical properties of a low voltage TiO_2 based varistor material.

EXPERIMENTAL DETAILS

The commercially purchased materials in the form of powder were TiO_2 (Merck), Bi_2O_3 (Aldrich) and WO_3 (Aldrich). The conventional method was used for powder preparation. The composition of the material for each sample is presented in Table 1. The powders were mixed by ball milling where ethanol was used as a solvent. The process was then followed by drying the slurry at 60^0C for 24 hours and was then followed by sieving. The green powder was then compacted using a hydraulic press machine with 2.76MPa into a disc of 20mm diameter. These green pellets were sintered at a temperature of 1350^oC with a holding time of two hours. Fired pellets were polished using different grades of SiC paper. Microstructural analysis was conducted using a scanning electron microscope (SEM), model S-3400N, to analyze grain size and porosity. The samples were coated with Au for SEM. The average grain size was calculated using average grain intercept in Eq.(1).

$$AGI = \text{line length} / \text{number of intercepts} \qquad (1)$$

For electroding, silver paste was applied to both the flat surfaces of the disc and cured at 600^0C for 30 minutes. The samples were evaluated using a Keithley 2612A electrometer with a line frequency of 50Hz. The non-linear coefficient, clamping ratio and breakdown voltage were calculated from the I-V plot. The software used for I-V measurement was TSP Express. Power loss was also found using Keithley 2612A electrometer and was measured at 80% of the breakdown voltage. Clamping efficiency was calculated by taking the two voltages at the non-linear region. Breakdown voltage was the electric field taken when the current was $1mA/cm^2$. Figure 1 shows the green and sample after silver paste was applied.

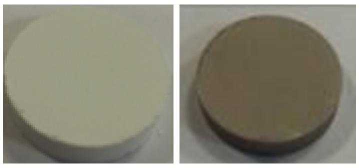

Figure 1. Green and fired sample with electrode.

Sample Identification	Composition of Raw Materials		
	TiO_2(%wt)	WO_3(%wt)	Bi_2O_3(%wt)
1	99.3	0.2	0.5
2	99.1	0.4	0.5
3	98.9	0.6	0.5
4	98.7	0.8	0.5
5	98.5	1.0	0.5

Table 1. Composition of raw materials.

RESULTS AND DISCUSSION

Effect of WO_3 and Bi_2O_3 on the Microstructure Properties

Average grain size is an important characteristic where grain growth plays an important role in electrical properties. Larger than average grain size is preferable for a low voltage varistor. Grain boundaries decrease the electrical conductivity of the material, thus higher than average grain size is essential to decrease the grain boundaries. However, a smaller crystallite size can improve the strength of the material. To achieve low breakdown voltage, a larger grain size is preferable. Decrease in average grain size is caused by degradation. The average grain size for this work ranged from 2.36µm to 5µm (Figure 2) which are considered to be average-large grain sizes. Increase in average grain size is due to TiO_2 which enhances grain size (Sabri et al., 2011). A large average grain size will facilitate low breakdown voltage because of the decrease in grain boundaries; less potential barrier is therefore formed. In the SEM photomicrographs in Figure 3, a small amount of porosity can be observed in Sample No 2. A reduced amount of porosity can also be linked to the improvement in terms of the strength of the material.

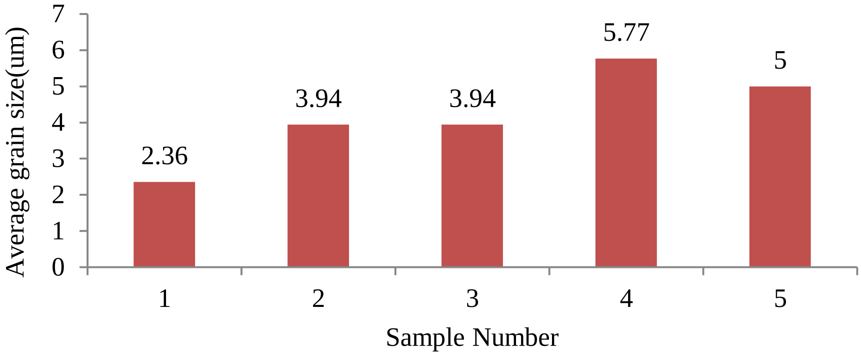

Figure 2. Average grain size with different concentrations of WO_3.

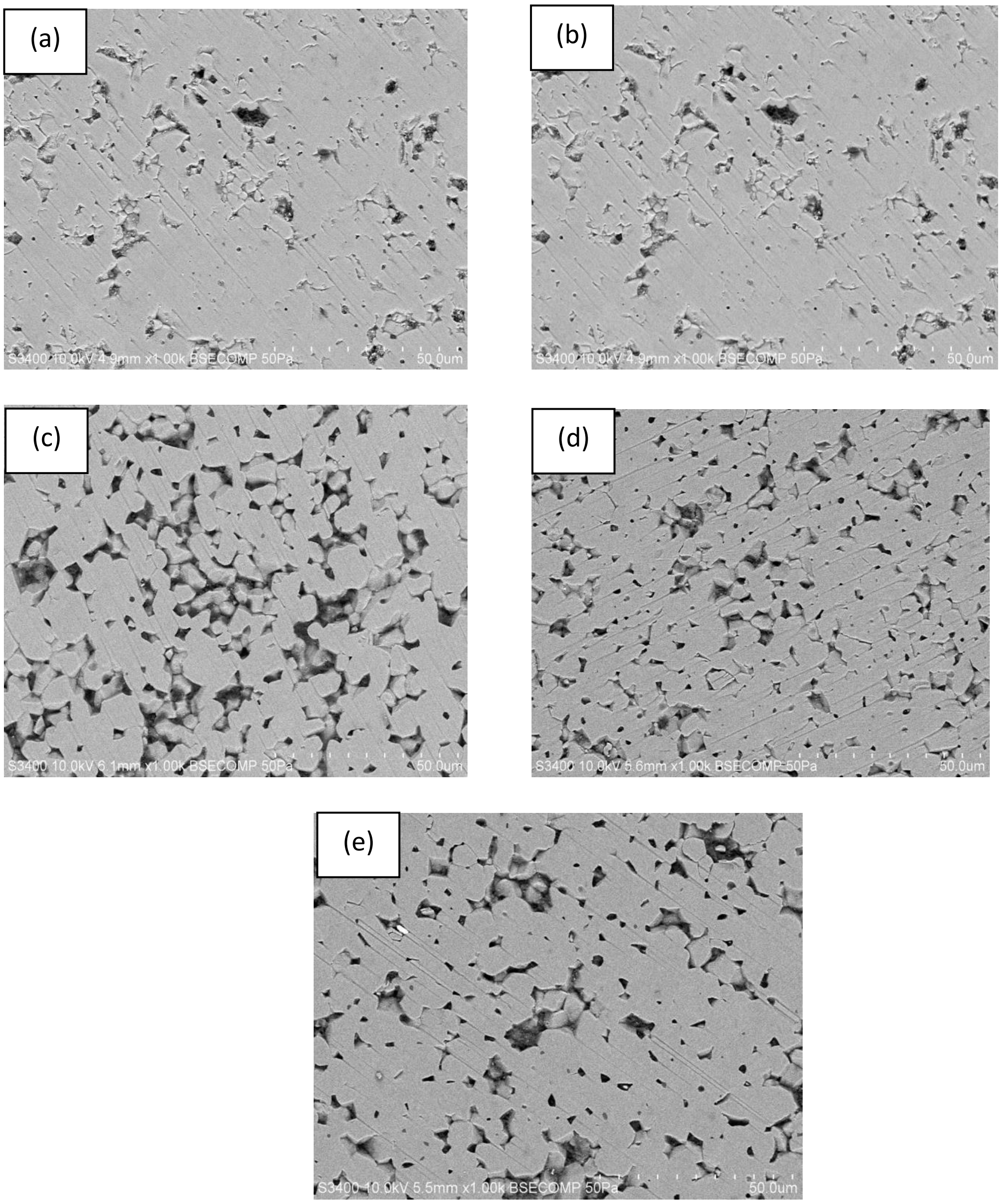

Figure 3. SEM photomicrographs with different concentrations of WO_3: (a) 0.2%WO_3, (b) 0.4%WO_3, (c) 0.6%WO_3, (d) 0.8%WO_3, (e) 1.0%WO_3

Effects of WO_3 and Bi_2O_3 on Electrical Properties

The non-linear coefficient varies with the current density and electric field. The non-linear coefficient was obtained from the non-linear region. The higher the non-linear coefficient, the better the varistor material for high surge transient voltage. I-V behavior is delineated in Figure 3. The non-linear coefficient can be obtained using Equation (2),

$$\alpha = \frac{\log(I_2) - \log(I_1)}{\log(V_2) - \log(V_1)} \tag{2}$$

where V_1 and V_2 are the correspondent voltages of I_1 and I_2 in the non-linear region.

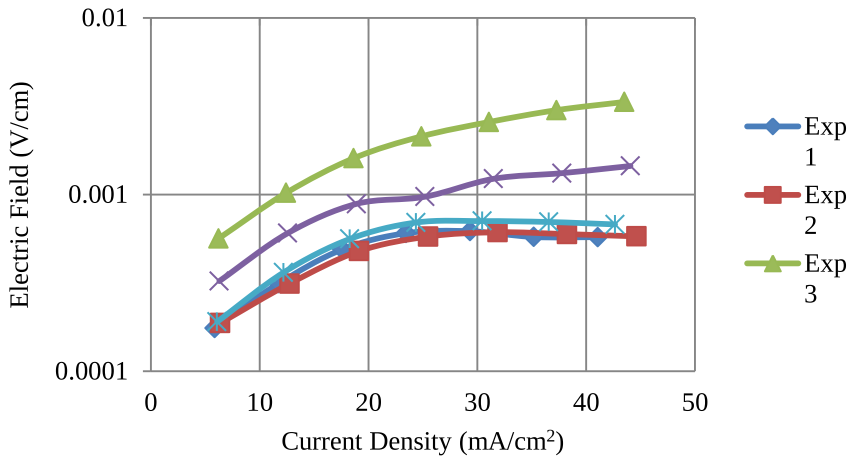

Figure 3. Electric field versus current density under different experimental conditions

According to Ravi and Date (2001), TiO_2 has a lower breakdown voltage compared to SnO_2. A low breakdown voltage is required for low voltage varistors which have been popularly used, due to low voltage applications. Leakage current determines the degree of degradation, and wattage loss is a good guide to determine the current leakage. Watt loss results from continuous leakage current. Clamping efficiency, non-linear coefficient and breakdown voltage was determined from the I-V plot. Clamping efficiency is defined as the ratio of voltages in the non-linear region and can be calculated as follows: clamping efficiency= V_2/V_1; where V_2 is the voltage per unit length at current density I_2 and V_1 is the voltage per unit length at current density I_1. The device will function better with lower clamp. A detailed analysis is shown in Table 2 where the non-linear coefficient, clamping efficiency, breakdown voltage and watt loss of each experiment are given.

Table 2. Electrical performance of samples under different experimental conditions

Sample Number	α	Clamping Efficiency	*Eb*(V/cm)	Power Loss (mW)
1	2.7	4.86	0.000294	0.00195
2	5.1	1.92	0.00022	0.0011
3	1.2	3.66	0.000323	0.001
4	2.1	2.67	0.000334	0.001
5	4.9	1.94	0.000237	0.001433

From Table 2, it can be seen that 99.1% TiO_2, 0.4% WO_3, and 0.5% Bi_2O_3 had the highest non-linear coefficient, lowest clamping efficiency and the lowest breakdown voltage. The breakdown voltage and power loss are low under all experimental conditions. Low power loss indicates that the semiconducting device will heat up less under steady state operation, thereby increasing the life of device. It was observed that the addition of WO_3 and Bi_2O_3 influenced the microstructure and electrical properties. The non-linear coefficient is higher compared to that of previous researchers where the addition of Nb, Ba to TiO_2 base varsitor was 3 (Sousa, Leite, Varela, & Longo, 2002).

CONCLUSIONS

The TiO_2 based varistor material doped with WO_3 and a fixed percent of Bi_2O_3 influenced microstructure and electrical properties. Relatively low clamping efficiency, higher non-linear coefficient, low breakdown voltage and less power loss was achieved when the varistor composition was 99.1% TiO_2, 0.4% WO_3, and 0.5% Bi_2O_3. The SEM micrograph indicated that porosity was low for the samples prepared under the same conditions. The average grain size was higher under this condition, which resulted in a lower breakdown voltage and thus made it suitable for low voltage applications. Reduced power loss also indicated a lesser leakage current, which is beneficial for steady state operation as it will cause less heating in continuous use. The large average grain found in this investigation would facilitate the use of TiO_2 for low voltage varistor application. The addition of 0.5% Bi_2O_3 and 0.4% WO_3 can thus yield optimum results for a low voltage TiO_2 based varistor.

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