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Short communication

Varistors based on Ta-doped TiO_2

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Abstract

The nonlinear current (*I*)–voltage (*V*) characteristics of titanium dioxide are examined when doped with small quantities (0.05–0.5 at.%) of tantalum pentaoxide. For optimum compositions, the nonlinear coefficients are found to be in the range of 25–30 and the breakdown field strength (E_B) is ~4000 V/cm. The obtained α- and E_B-values are higher than the previously reported values for TiO_2 ceramics. The acceptor like surface states at the grain boundary adsorb oxygen during sintering and cooling, leading to formation of grain boundary barrier. The grain boundary barrier height (Φ_B) is calculated using Schottky equation.

Keywords: D. TiO_2; E. Varistor; Ceramics; Oxides; Schottky barrier

1. Introduction

Varistors are electroceramic devices that show nonlinear electrical property. They are widely used to protect electrical and electronic equipment against transient overvoltages. Their current (*I*)–voltage (*V*) characteristics can be expressed by $J = (E/C)^{\alpha}$, where J is current density, E is applied field strength, C is the proportionality constant and α is the nonlinear coefficient. The most commonly used commercial varistors are ZnO-based compositions [1,2]. It had been also already well established that the electrical nonlinearity in polycrystalline ZnO ceramics arises from grain boundary phenomenon. ZnO varistors contain small quantities of a variety of metal oxides in order to get high α-values. It will be very advantageous, if we could develop binary system with desired nonlinear electrical properties. Hence we have attempted to prepare varistors based on TiO_2 with single additive. TiO_2 is a versatile material that has wide range of applications ranging from pigments, photocatalyst and capacitors [3]. Yan and Rhodes [4] reported that (Nb, Ba) doped TiO_2 ceramics had useful varistor properties with α of about 4. This was followed by a number of investigations [5–8] reporting varistor action in TiO_2 with low breakdown field strengths. Here we report the nonlinear *I*–*V* characteristics of tantalum doped TiO_2 ceramics. Unlike SnO_2, it does not need any additives for densification. There are also reports on non-ohmic behavior of SnO_2 [9–12], when properly doped with optimum quantity of aliovalent ions. Bueno et al. [13] have reported low voltage varistors based on $Sn_{1-x}Ti_xO_2$ ceramics doped with cobalt and niobium in very small quantities.

2. Experimental

The samples used in all the experiments were purchased from commercial source (Loba Chemie) and of GR grade (purity ~99.9%). Samples are prepared by standard ceramic technique. TiO_2 (average particle size 0.7 μm) and Ta_2O_5 (average particle size 0.5 μm) are weighed in required ratio ($(100 - X)TiO_2 + X$ (Ta), where $X = 0.01$, 0.05 0.1 and 0.5, all in at.%) and mixed well with acetone and ground for several hours with a agate mortar and pestle. The powder samples are mixed with few drops of a binder (poly vinyl alcohol, 1 wt.% solution) and pelletized (15 mm diameter, 2 mm thickness, at 200 MPa). The green pellets were sintered in air at 1573 K for 4 h. The density of the pellets were measured by Archimedes method and they are >93% of the theoretical value. The phase contents and lattice parameters were studied using Philips powder X-ray

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diffractometer. For lattice parameter and interplanar distance (d) calculation, the samples were scanned in the 2θ range of 20–60° for the period of 5 s in the step scan mode. Silicon was used as an internal standard. Least squares method was employed to determine the lattice parameters. The sintered pellets were polished and low temperature curing silver paint is applied on its surfaces. The pellets were cured at 873 K for 30 min. The *I–V* curves are measured using a Keithley electrometer 6517 A. It also contains a built in 1-kV dc power supply so that there is no need of external power supply in the circuit. The current–voltage curves were plotted on log–log scale and the slope of the curve gives the value of α. The important parameter, E_B, breakdown field strength is taken as the field applied when current flowing through the varistor is 1 mA/cm^2. Since Schottky type grain boundary barriers are present in the present samples the current density in ohmic region of varistor is related to the electric field and the temperature given by equation [11].

$$J = AT^2 \exp\left[\frac{(\beta E^{1/2} - \Phi_B)}{kT}\right] \quad (1)$$

where A equal to $4\rho emk^2/h^3$, is the Richardson's constant, ρ is the density of titanium dioxide, e is the electron charge, m is electron mass, k is the Boltzmann constant, h is the Plank constant, Φ_B is the interface barrier height, and β is a constant related to the relationship:

$$\frac{\beta \alpha 1}{r \omega} \quad (2)$$

where r is the grain number per unit length and ω is the barrier width. Measuring the current density in ohmic region and keeping the temperature of the tested varistor constant, for two different applied fields, the equations are:

$$J_1 = AT^2 \exp\left[\frac{(\beta E_1^{1/2} - \Phi_B)}{kT}\right] \quad (3)$$

$$J_2 = AT^2 \exp\left[\frac{(\beta E_2^{1/2} - \Phi_B)}{kT}\right] \quad (4)$$

The values of Φ_B and β can be calculated from above equations. The microstructure of the sintered pellets was observed using a Leica Cambridge 440 microscope. The average grain size was calculated from linear intercept method. A LCR meter was used to measure the room temperature dielectric constant of the sintered samples at 1 kHz.

3. Results and discussion

All the samples doped with tantalum pentoxide are single phase rutile by X-ray diffraction studies (XRD not shown). The lattice parameters calculated by least square fit are, a = 4.568 Å and c = 2.949 Å. It is to be noted that amount of incorporation of tantalum is too small to be detected by XRD. When starting powders are anatase phase, the sintered pellet always contained cracks. This may be due to the change in unit cell dimensions during phase transition between anatase and rutile occurring around 1000 K. Hence all the samples used for *I–V* measurement are prepared from rutile powders. Rutile powders are obtained by annealing TiO_2 powders at 1000 K for 24 h. Fig. 1 shows the microstructure of the fractured surface of sintered pellets. The average grain size obtained by the linear intercept method is in the range of 4–5 μm. The *I–V* relations for tantalum doped samples are illustrated in Fig. 2. When tantalum content is other than 0.1 at.%, the samples become insulating. Only when tantalum content is around 0.1 at.%, the samples exhibited high nonlinear electrical behavior. The obtained α (=30) and E_B (=4000 V/cm) values are higher as compared to previously reported values for TiO_2 ceramics [4–7]. In general only low voltage varistors based on TiO_2 are reported [4–8]. This is because higher grain growth is obtained during sintering. But present results shows that for specific compositions based on TiO_2, high voltage varistors can also be obtained. The major advantage is for even for ZnO based varistors, a variety of metal oxides has to be added to get high α-values, whereas for the present samples only one additive is used. The measured dielectric constant is found to be 4500, which cannot be accounted for by either

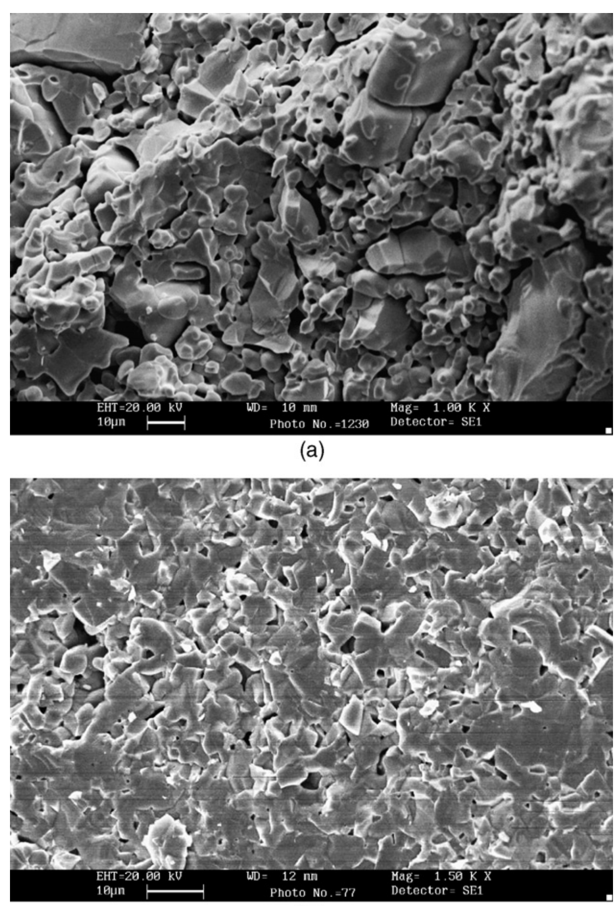

Fig. 1. Microstructure of: (a) 0.1 at.% and (b) 0.5 at.% Ta doped TiO_2.

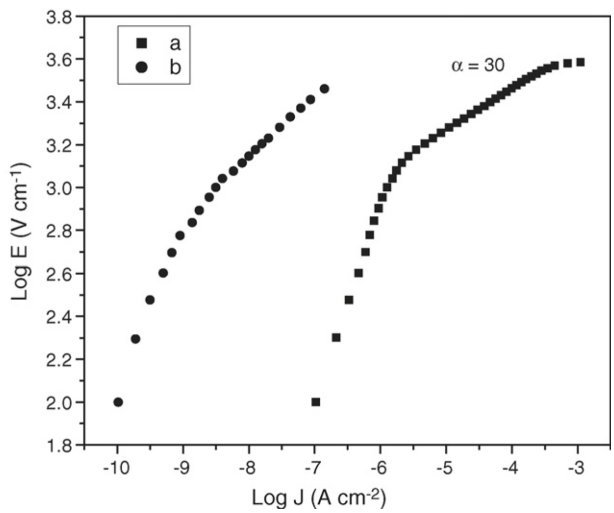

Fig. 2. The *I–V* characteristics of: (a) 0.1 at.% and (b) 0.5 at.% Ta doped TiO_2.

TiO_2 ($\varepsilon = 80$) or the intergranular materials. The high permittivity of the ceramic arises [17], from the fact that the resistivity of TiO_2 grains is much lower than that of the grain boundary layers, so the entire voltage is sustained across narrow intergranular regions and the polarization is large. The effective dielectric constant of the ceramic is then given by

$$\varepsilon_r = \varepsilon_b \frac{d}{t} \tag{5}$$

where ε_b is the permittivity of the TiO_2, d is the size of the cube grains and t is the mean thickness of the insulation barrier.

The varistor action observed in polycrystalline ZnO ceramics is explained by the presence of Schottky type energy barrier at the grain boundaries. In analogy to the model proposed by Gupta and Carlson [14] for a ZnO based varistor and by Bueno et al. [15,16] for SnO_2 varistor, the following model based on defect associated with grain boundary barrier as shown schematically in Fig. 3 can be proposed. A depletion layer is formed by positively charged defects induced by the incorporation of tantalum. A negative interface composed of O' and O'' is formed during sintering and cooling which is necessary to compensate the positive depletion layer. The ionic radius of Ta^{5+} ion being similar to Ti^{4+}, it forms solid solution with TiO_2 in small quantities and lead to increase or decrease in the grain conductivity depending upon compensation

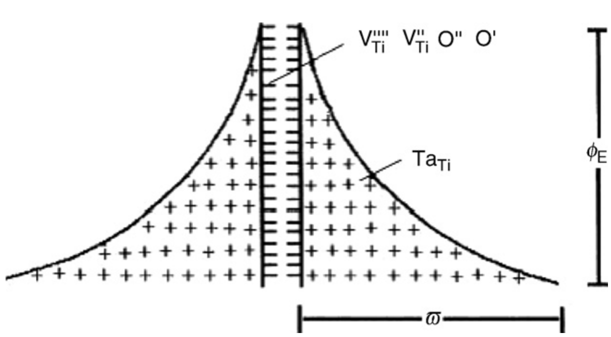

Fig. 3. Schematic diagram of grain boundary barrier.

mechanisms as discussed in [10]. At the same time the presence of Ta generates abundant molecular oxygen according to the reaction

$$Ta_2O_5 + TiO_2 \rightarrow 2Ta_{Ti} + 2e + \tfrac{1}{2}O_2 + 6O_o \tag{6}$$

$$2Ta_2O_5 + TiO_2 \rightarrow 4Ta_{Ti} + V''''_{Ti} + 12O_o \tag{7}$$

which is adsorbed at the interfaces and becomes O' and O'' according to reaction,

$$O_2(g) \rightarrow 2O_{ad} \tag{8}$$

$$2O_{ad} + V''''_{Ti} \rightarrow 2O' + V''_{Ti} \tag{9}$$

$$O_{ad} + V''''_{Ti} \rightarrow O'' + V''_{Ti} \tag{10}$$

This model is very similar to that reported by Su et al. [5] and only difference is that here defects are generated by the additive tantalum and not by tungsten. The grain boundary height (Φ_B) calculated using the Eqs. (3) and (4) for the present samples is 0.85 eV.

4. Conclusions

Addition of small quantities of tantalum pentoxide into titania leads to highly nonlinear electrical characteristics. It has potential applications for high voltage surge protection as found ZnO ceramics. It contains only single element as compared to commercial ZnO varistor compositions with many additives. At present investigations are underway to study the influence of barium or lanthanum on these ceramics.

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