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Nanosecond reversible solid state switches capable of handling MJ of energy

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Abstract

The theoretical applicability of the Schottky thermionic emission model to electronic transport at tin dioxide grain boundaries is addressed. Firstly, the theoretical behaviour of the barrier height $\phi_{(v)}$ versus applied voltage V is determined for a single grain boundary. Next we predict the current density–voltage characteristics as a function of temperature, demonstrating good correlation between experimental and theoretical results. The model carried out has the advantage that it contains no adjustable parameters. Agreement with experimental results from optimised polycrystalline ceramics gives strong evidence for the double-depletion-layer/thermionic-emission model. Moreover, this study emphasises the importance of the direct large-bandgap of doped SnO_2 in surge-arrester applications, and gives credibility to the analogy between the apparent behaviour of doped SnO_2 and doped ZnO varistors. Doped polycrystalline tin oxide ceramic is the first material to compete with doped ZnO in the medium and high voltage applications for surge arresters.

Keywords: SnO_2; Varistor; Surge arrester

1. Introduction

Varistors are nowadays currently used as voltage spike suppressors in electronic, electro-technical and tactical devices. The word varistor comes from a portmanteau of the words variable and resistor. It is a passive component that displays a non-ohmic, current–voltage behaviour, which may be used as clamping device to limit a voltage to defined level.[1] Commercial varistors are based on both SiC and ZnO, in spite of the fact that ZnO exhibits substantially and indisputably higher performances. Recently in 1995[2] SnO_2-based ceramics have found new applications as varistors, although studies on the electrical properties of such non-linear semiconductor devices were already underway in Russia in the early 1970s.[3] More than 300 scientific papers, all devoted to doped SnO_2 varistors, have been since published. (SciFinder bibliography analysis over the period 1995–2009.)

In ZnO varistors, the so-called varistor effect is controlled electrically by grain boundaries that are tuned by composition, microstructure and sintered material processing. The model of Greuter et al.[4–7] offers a good description of the highly non-linear properties of the electrically active grain boundaries of correctly doped and manufactured ZnO ceramics. The essential principle underlying varistor action relies on an analogy between the electronic behaviour of a ceramic grain boundary and a metal–semiconductor junction.

The metal–semiconductor (M-SC) junction is the simplest unipolar device at the base of a great number of more complex structures. In this type of device, only one type of particle (electron or hole) assumes the role of charge carrier and determines the operating conditions of the device. Generally, application of a potential difference across M-SC junction produces a non-symmetrical I–V characteristic, which is useful in semiconductor electronics applications such as Schottky diodes. In actual fact, however Schottky barriers appear at most semiconductor interfaces: solid–air interface or grain boundaries. The Schottky barrier corresponds to the energy barrier to which a

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free electron moving towards the semiconductor is confronted. The origin of theses electrostatic barriers at the interfaces stems from lattice mismatches, defect concentration and dopant segregation at the grain surface and/or grain boundary. In the case of grain boundaries, the electrical behaviour is symmetrical and can be described as two Schottky barriers connected back-to-back.

However in the specific case of both ZnO and SnO_2, an unexpectedly high level of non-linearity and a high-energy handling capability are observed. The last property is due to the ceramic polycrystalline microstructure, although the physical origin is yet not very well understood.[1,8,9] Concerning the non-linearity performance, values of α up to 100 have been reported.[1,10]

The first high voltage investigations have been released recently.[11,12] These first studies produced encouraging results, but need to be improved to compete with ZnO polycrystalline material. The purpose of this study is to report both on one of the best formulations obtained so far and to give, for the first time, a comprehensive thermionic emission model applied to an electrically active grain boundary in doped SnO_2.

2. Experimental

The oxides used in this study were SnO_2 (Alfa Aesar, 99.9%), Co_3O_4 (Alfa Aesar, 99.7%), Nb_2O_5 (Aldrich, 99.9%), Cr_2O_3 (Alpha Aesar, 99%), B_2O_3 (Alfa Aesar, 99.98%), Ta_2O_5 (Aldrich, 99.99%), Tl_2O_3 (Fluka, 99%) and Al_2O_3 (Aldrich, 98%).

The oxides were mixed in appropriate proportions and ball-milled in agate bottles for 1 h.

The oxide powders were then mixed with a polyvinyl alcohol binder granulated and pressed into pellet shapes. The powders were uniaxially constrained at a pressure of 7×10^9 Pa during few seconds. Pellets with a diameter of about 10 mm and a thickness of about 2 mm were then sintered in ambient air atmosphere at 1623 K for 2 h. They were heated at a rate of 120 K h^{-1} to the sintering and room temperatures. Densities were determined by geometrical measurement of the volume and by weighing the pellets using an analytical balance. The relative density of the specimens was calculated starting from the following formula:

$$\text{Relative density}\,(\%) = 100\frac{\rho}{\rho_{th}} \quad (1)$$

with ρ = apparent density of the pellet (g cm^{-3}), $\rho_{th} = 6.95$ g cm^{-3}; theoretical density of SnO_2 calculated from a tetragonal SnO_2 structure with cell parameters: $a = 0.4738$ nm and $c = 3.185$ nm.[13]

Microstructure characterisation of sintered samples was made by scanning electron microscopy (Hitachi S 800 and XL30 ESEM Philips coupled with energy dispersive spectroscopy (EDS – EDAX)). X-ray patterns on ground sintered ceramics were recorded on a Bruker D8 Advance diffractometer ($CuK_{\alpha 1,\alpha 2}$) equipped with a Vantec detector and a spinner.

The average size of the grains was measured by Mendelson's method[14] as per the recommended formula: $G = 1.56\,L$, with L: the average length between grains.

For the electrical measurements, silver contacts were deposited on the sample surfaces, after which the pellets were heat-treated at 873 K for several minutes. To determine the electrical properties as a function of temperature a special sample holder was built and attached to an electrical source and two digital multimeters for current higher than 1 mA cm^{-2}, the current–voltage measurements were taken using a high voltage-measuring unit using a current generator which delivers a 8/20 μs impulse current with a peak short-circuit of 6 kA. The non-linear coefficient was obtained by linear regression of the experimental points using a logarithmic scale around 1 mA cm^{-2} and the breakdown electrical field was calculated at this current density. The non-linear coefficient α, for all the samples studied, was estimated between two desired magnitudes of current and corresponding voltage by

$$\alpha = \log_{10}\left(\frac{E_{1\text{mAcm}^{-2}}}{E_{0.1\text{mAcm}^{-2}}}\right) \quad (2)$$

where $E_{0.1\text{mAcm}^{-2}}$ and $E_{1\text{mAcm}^{-2}}$ stand for the voltage fields at current densities 0.1 mA cm^{-2} and 1 mA cm^{-2}, respectively.

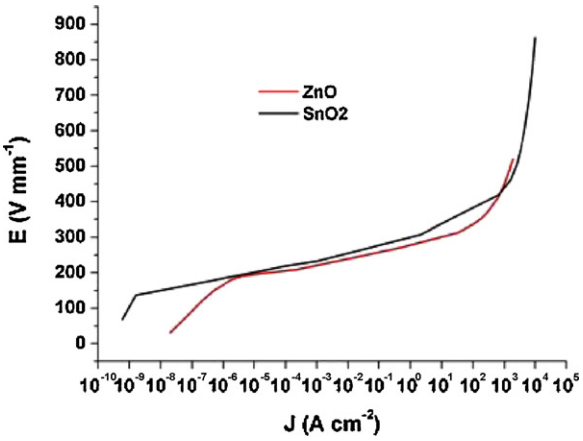

Fig. 1. Electric field according to the current density for doped dioxide varistors sintered at 1350 °C during 2 h after a cooling of 120 K h^{-1}. For comparison purpose the electrical behaviour of a doped-ZnO commercial ceramic is reported.

3. Results and discussion

3.1. Electronic parameters describing the potential barrier at the grain boundary

After many empirical tests on ceramic formulations that foster on both large non-linearity coefficient and absorption capability we found that the composition [97.7145%$_{wt}$ SnO_2 + 0.5355%$_{wt}$ Co_3O_4 + 0.5%$_{wt}$ Nb_2O_5 + 0.25%$_{wt}$ Cr_2O_3 + 0.1%$_{wt}$ B_2O_3 + 0.25%$_{wt}$ Ta_2O_5 + 1%$_{wt}$ $Tl(NO_3)_3$, $3H_2O$ + 0.05%$_{wt}$ $Al(NO_3)_3$, $9H_2O$] exhibits the largest range of operation. As depicted in Fig. 1, current density versus applied field E, there is an enormous variation in current (a factor of 10^{12}: 10^{-9} to 10^3 A cm^{-2}) while the applied field varies only about a factor of 3 (150–400 V mm^{-1}).

By conducting the electric tests and knowing the microstructure, we can estimate a potential barrier per grain. In fact, if we accept that ceramics are homogeneous with grains of the same