

ON THE QUEST OF NEW CERAMICS FOR VARISTORS (*)

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ABSTRACT—The varistor effect is described in the Bi doped ZnO and the theory which attributes this effect to a space-charge layer between semiconducting grains is briefly related. The structure of a single-contact varistor is presented. The ideas underlying a quest for new ceramics, which might show the varistor effect, are expressed. The results obtained with sandwich-type structures, either Li doped NiO or Ti doped Fe_2O_3 , having intermediate foils of Bi, Sb, Cr, Mn and Co oxides are presented.

1 — INTRODUCTION

The varistor effect in bismuth-doped zinc oxide.

In some polycrystalline ceramics, such as silicon carbide and zinc oxide with small additions of certain oxides [1, 2, 3], one observes the so-called varistor effect, characterized by a rectifier, bidirectional effect through several orders of magnitude of the current intensity, as illustrated in Fig. 1. At low voltage, the material shows great ohmic resistance; at a somewhat higher voltage nonlinearity sets in, a breakdown occurs and the current intensity increases very steeply with the voltage, according to a relation usually described by a power law, $I = k V^n$; for still higher voltages, we come to the up-turn region and the resistance takes again ohmic character.

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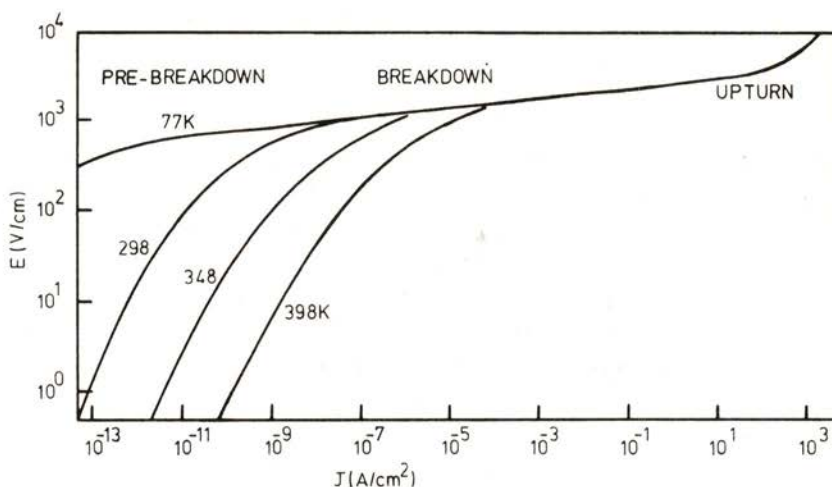


Fig. 1 — Current voltage characteristic of a bismuth doped zinc oxide varistor.

The varistor effect is generally attributed to a boundary effect at the interface of the grains [2]. The microstructure of a zinc oxide varistor, which gives support to this interpretation, is shown in Fig. 2 [4]. It can be seen that between the semiconducting

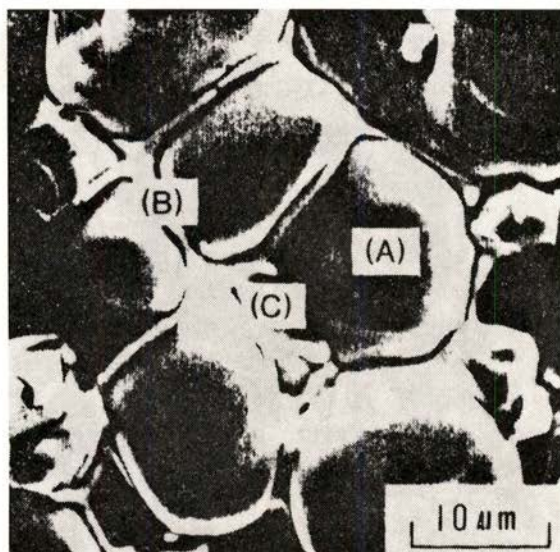


Fig. 2 — Microstructure of zinc oxide doped with bismuth [4].

grains of zinc oxide with dimensions of order $10 \mu\text{m}$ (A), there is a layer rich in bismuth (B), and regions with spinel (C). The existence of bismuth is generally considered fundamental in order to allow, during the sinterization, that the grains have their surfaces wetted, thus promoting their oxidation and, consequently, the intergranular fixation, as oxides, of other elements which are added in green (Bi_2O_3 , Co_2O_4 , MnO , Cr_2O_3 , ...). The substitution of a divalent zinc ion for a trivalent ion gives rise to an extra positive charge, 50 Angstroms wide, internally adjacent to the grain surface, which implies the formation of a negative charge in the intergranular region. This corresponds to back-to-back Schottky diodes, consisting of a charged interface in association with a space-charge layer, which has both ionic and electronic parts.

A metal-oxide varistor is very often described by the simple equivalent circuit shown in Fig. 3. A pure capacitance, C_p , in parallel with a voltage dependent resistance, R_p , represents the intergranular layers, while r_g is the resistance of the semiconducting grains. For low applied voltages, R_p exhibits an Ohmic behaviour.

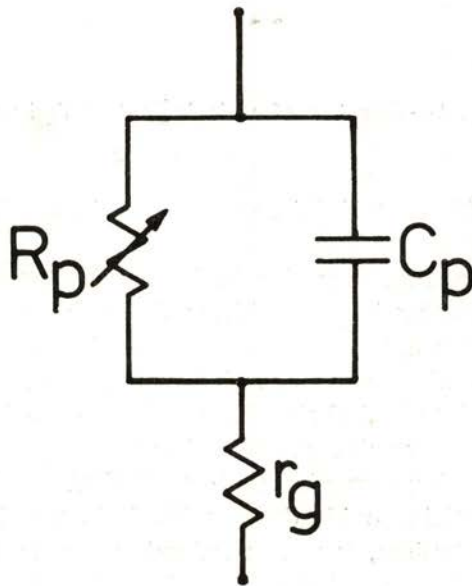


Fig. 3—Simple equivalent circuit representing a metal-oxide varistor.

Single-Contact Varistor.

In order to reproduce the structure "grain-intergranular region-grain", it was thought to make a single-contact varistor. This consists (see Fig. 4) of a structure of two slices of zinc oxide doped with other oxides in very small percentages [5], or of zinc oxide single-crystals [6], between which a foil with a thickness of the order of $100\ \mu\text{m}$ is placed. This assembly is sintered under pressure, leading, in a controlled way, to a single contact of sequence zinc oxide grain (semiconductor) — potential barrier — zinc oxide grain (semiconductor).

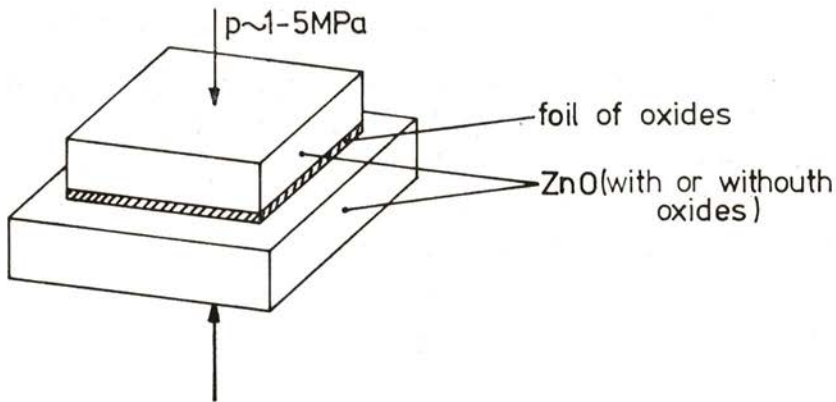


Fig. 4 — Structure of a Single-Contact Varistor.

2 — LOOKING FOR NEW SUBSTANCES FOR VARISTORS

The quest of new ceramics, which exhibit the varistor effect, was mainly influenced by two ideas: 1) to find an oxide, simple or adequately doped, which manifests a semiconducting behaviour and has a convenient charge carrier concentration, and 2) to discover the additives and their adequate concentrations which can originate an intergranular potential barrier.

Semiconducting ceramics with controlled carrier concentration, based on nickel oxide doped with lithium and ferrous oxide doped with titanium, were obtained after suitable thermal treatments. In the formation of the foil, to be placed between the semiconducting oxide slices, oxides were used which have a metal

with a) valence different from that of the metal in the oxide of the grains (Ni or Fe) and b) a greater atomic diameter. It is supposed that, for reasons of minimum of free energy, the impurities will segregate predominantly at the grain interface [7] originating, in that way, a space charge layer, already referred to in Section 1.

3 — EXPERIMENTAL

The approximate dimensions of the slices of semiconductor ceramics, with polished or unpolished faces, were $1.5 \times 1.5 \times 1.0$ mm³. To prepare the foils, a mixture of 2 grams of the chosen oxides, dispersed in 2 grams of deionized water, was ground, and 3 grams of an organic binder (Poliviol at 20 %) were added. The resulting emulsion was afterwards conveniently stirred. A paste was spread on a smooth sheet of glass (or plastic) with a brass roller whose surface was completely full of grooves. The depth of these grooves is the same as that of the required foil. We have used foils 250 μ m thick. A sandwich was formed by inserting this thin foil between a pair of the ZnO plates.

This assembly was sintered either in a horizontal or a vertical oven. In the horizontal oven, the pressure was obtained through a spring, while, in the vertical one, this was achieved by means of weights. Temperatures, durations of sintering, as well as the used pressure, are reported in Table I.

To get the characteristics $I = I(V)$, good ohmic contacts with the ceramics were needed, for which we have applied the indium-gallium alloy at the eutectic point. The current intensity was measured with an electrometer (Model 610, of Keithley Instruments). For current intensities above 10^{-8} — 10^{-7} Ampères the measurements were made using pulses to avoid self-heating which causes thermal instability (thermal run-away).

4 — RESULTS

We have tried to make varistors by using ceramics of nickel oxide doped with lithium and of ferrous oxide doped with titanium. The foils we employed were of: oxides of Bi and Ba in the proportion of Bi : Ba = 2 : 1; and oxides of Sb, Bi, Cr, Mn and Co in the proportion of Sb : Bi : Cr : Mn : Co = 4 : 2 : 2 : 1 : 1.

TABLE I

Attempt Nr.	Slices	State of the faces	Foil	Thermal Treatment	Results
1	NiO, 4 % Li	As cut	Bi:Ba = 2:1	T = 1000°C, p = 1.3 MPa, t = 1 hr	Unsuccessful
2	NiO, 4 % Li	Idem	Idem	(T = 1000°C, p = 2.6 MPa, t = 1 hr 30 mn) + (T = 1100°C, p = 2.6 MPa, t = 1 hr)	Idem
3	NiO, 4 % Li	Idem	Idem	(T = 1120°C, p = 1.0 MPa, t = 1 hr) + (T = 1200°C, p = 0 Pa, t = 1 hr)	Mechanically stable
4	Fe ₂ O ₃ , 1.5 % Ti	Polished	Sb:Bi:Cr:Mn:Co = 4:2:2:1:1	T = 960°C, p = 1.6 MPa, t = 1 hr	Unsuccessful
5	Fe ₂ O ₃ , 1.5 % Ti	Idem	Idem	T = 1030°C, p = 1.6 MPa, t = 1 hr	Weak cohesion
6	Fe ₂ O ₃ , 1.5 % Ti	Idem	Idem	T = 1050°C, p = 3.0 MPa, t = 1 hr 40 mn	Mechanically stable
7	Fe ₂ O ₃ , 1.5 % Ti	Idem	Idem	As the last attempt + (T = 1150°C, p = 0 Pa, t = 1 hr 40 mn)	Idem
8	Fe ₂ O ₃ , 1.5 % Ti	Idem	Idem	As the last attempt + (T = 1150°C, p = 3.0 Pa, t = 45 mn)	Idem
9	Fe ₂ O ₃ , 0.5 % Ti	As cut	Idem	T = 950°C, p = 5.0 MPa, t = 1 hr	Unsuccessful
10	Fe ₂ O ₃ , 0.5 % Ti	Idem	Idem	T = 1050°C, p = 5.0 MPa, t = 1 hr	Idem
11	Fe ₂ O ₃ , 0.5 % Ti	Idem	Idem	T = 1200°C, p = 0.2 MPa, t = 18 hr	Mechanically stable
12	Fe ₂ O ₃ , 0.2 % Ti	Idem	Idem	T = 1200°C, p = 0.2 MPa, t = 16 hr	Idem
13	Fe ₂ O ₃ , 0.5 % Ti	Polished	Idem	T = 1050°C, p = 5.0 MPa, t = 1 hr	Unsuccessful
14	Fe ₂ O ₃ , 0.5 % Ti	Idem	Idem	T = 1100°C, p = 5.0 MPa, t = 1 hr	Idem
15	Fe ₂ O ₃ , 0.5 % Ti	Idem	Idem	T = 1050°C, p = 1.7 MPa, t = 1 hr	Mechanically rather stable

A preliminary objective, of obvious and fundamental importance, is concerned with the mechanical stability of the structure. The attempts which were made and their results are concisely shown in Table I. We can conclude, although cautiously waiting further trials, that the duration of the treatment and the smoothness of the faces will favour mechanical stability. As to the influence of the pressure it seems there exists a recommended range of values.

On the mechanically stable structures, measurements were made which led to the establishment of the $I = I(V)$ characteristics. In Fig. 5 it is shown the characteristic of the structure

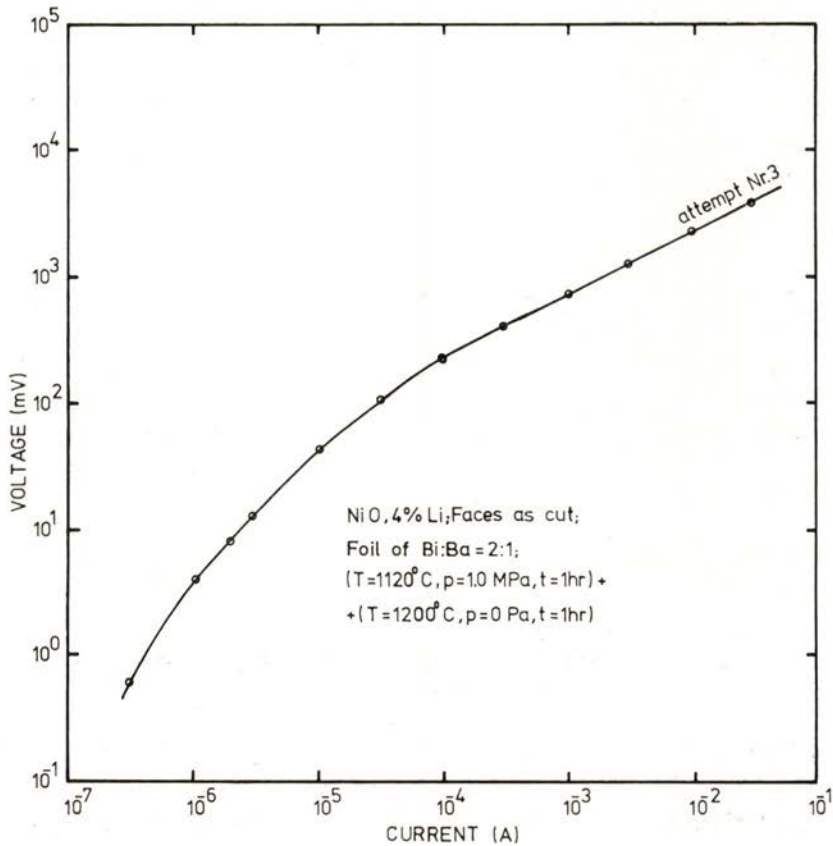


Fig. 5 — Characteristic $I = I(V)$ of the structure of Attempt Nr. 3.

corresponding to attempt Nr. 3 (Ni O, 4 % Li; foil Bi : Ba = 2 : 1) . In Fig. 6, can be seen the characteristics of structures where the slices were made of Fe_2O_3 , with 1.5 % (Attempt Nr. 6), 0.5 % (attempts Nrs. 11 and 15) or 0.2 % (Attempt Nr. 12) Ti, the foil being, in all cases, formed with oxides of elements in the proportions Sb : Bi : Cr : Mn : Co = 4 : 2 : 2 : 1 : 1 .

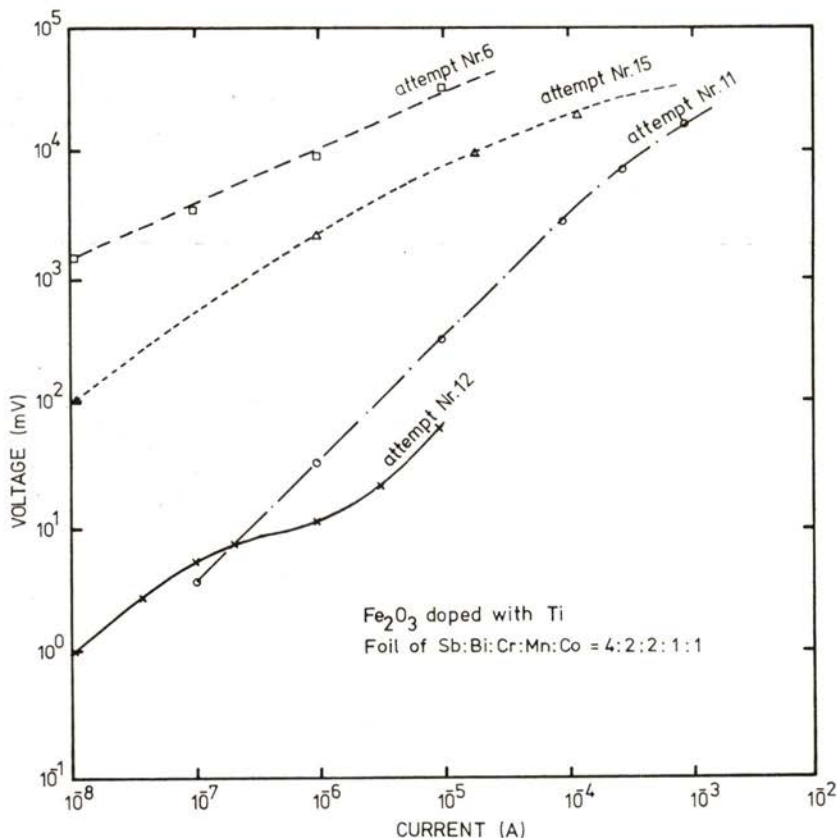


Fig. 6 — Characteristics $I = I(V)$ of the structures of Attempts Nrs. 6, 11, 12 and 15.

Taking as a measure of the nonlinearity the value of the exponent α (in the relation $I = k V^\alpha$) we have, for each of the characteristics, the following maximum values: $\alpha_m = 2$ (Attempt Nr. 3); $\alpha_m = 2.2$ (Attempt Nr. 6); $\alpha_m = 1.4$ (Attempt Nr. 11); $\alpha_m = 4$ (Attempt Nr. 12) and $\alpha_m = 2.5$ (Attempt Nr. 15).

We consider our results rather promising, intending therefore to go on looking for new ceramics which exhibit the varistor effect.

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