NON-LINEAR RESISTOR OF SINTERED ZINC OXIDE

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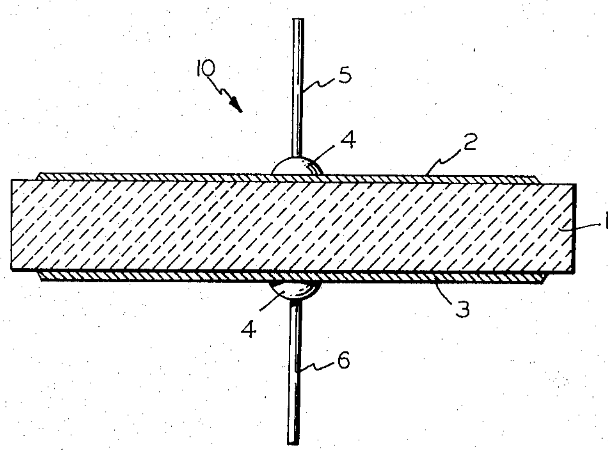

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NON-LINEAR RESISTOR OF SINTERED ZINC OXIDE

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ABSTRACT OF THE DISCLOSURE

A non-linear resistor. The resistor has a sintered disc of zinc oxide and two electrodes, one applied to each of the opposite surfaces of said sintered disc. One of said two electrodes is a silver electrode in non-ohmic contact with one of said opposite surfaces, and the other of said two electrodes in ohmic contact with another of said opposite surfaces.

This invention relates to non-linear resistors having non-ohmic resistance, and relates more particularly to varistors comprising a sintered disc of zinc oxide and two electrodes applied to opposite surfaces of said disc, one of said two electrodes being in ohmic contact therewith and the other of said two electrodes being in non-ohmic contact therewith.

Various non-linear resistors such as silicon carbide varistors, selenium or cuprous oxide rectifiers and germanium or silicon p-n junction diodes, are known. The electrical characteristics of such a non-linear resistor are expressed by the relation:

$$I=\left(\frac{V}{C}\right)^n$$

where V is the voltage across the resistor, I is the current flowing through the resistor, C is a constant corresponding to the voltage at a given current, and the exponent n is a numerical value greater than 1. The value of n is calculated by the following equation:

$$n=\frac{\log_{10}(I_2/I_1)}{\log_{10}(V_2/V_1)}$$

where V_1 and V_2 are the voltages at given currents I_1 and I_2, respectively. Conveniently, I_1 and I_2 are 10 ma. and 100 ma., respectively. The desired value of C depends upon the use to which the resistor is to be put. It is ordinarily desirable that the value of n be as large as possible since this exponent determines the degree to which the resistors depart from ohmic characteristics.

Silicon carbide varistors are most widely used as non-linear resistors and are manufactured by mixing fine particles of silicon carbide with water, ceramic binder and/or conductive material such as graphite or metal powder, pressing the mixture in a mold to the desired shape, and then drying and firing the pressed body in a non-oxidizing atmosphere. Silicon carbide varistors with conductive materials are characterized by a low electric resistance, i.e. a low value of C and a low value of n, whereas silicon carbide varistors without conductive materials have a high electric resistance, i.e. a high value of C and a high value of n. It has been difficult to manufacture silicon carbide varistors characterized by a high n and a low C. For example, silicon carbide varistors with graphite have been known to exhibit n-values from 2.5 to 3.3 and C-values from 6 to 13 at a given current of 100 ma., and silicon carbide varistors without graphite have n-values from 4 to 7 and C-values from 30 to 800 at a given current

of 1 ma. for a given size of varistor, e.g. 30 mm. in diameter and 1 mm. in thickness.

Conventional rectifiers comprising selenium or cuprous oxide have an n-value less than 3 and a C-value of 5 to 10 at a given current of 100 ma. for a specimen size of 20 mm. in diameter. In this case, the thickness of the sample does not affect the C-value.

A germanium or silicon p-n junction resistor has an extremely high value of n but its C-value is constant, e.g. on the order of 0.3 or 0.7 at a given current of 100 ma., because its diffusion voltage for the V–I characteristics is constant and can not be changed greatly. It is necessary for obtaining a desirable C-value to combine several diodes in series and/or in parallel. Another disadvantage of such diodes is the complicated steps involved in their manufacture, with resultant high cost. As a practical matter, the use of diode resistors is not widespread at the present in view of their high cost even though they have a high value of n.

An object of this invention is to provide a non-linear resistor having a high value of n and a low value of C.

A further object of this invention is to provide a non-linear resistor capable of being made by a simple manufacturing method and hence at a low cost.

A further object of this invention is to provide a non-linear resistor characterized by a high stability with respect to temperature, humidity and electric load.

Another object of this invention is to provide a non-linear resistor, the C-value of which can be controlled.

These objects are accomplished by providing a non-linear resistor comprising a sintered disc of zinc oxide and two electrodes, one applied to each of the opposite surfaces of said sintered disc, one of said two electrodes being a silver electrode in non-ohmic contact with one of said opposite surfaces, and the other of said two electrodes being in ohmic contact with another of said opposite surfaces.

These and other objects of the invention will become apparent upon consideration of the following description taken together with the accompanying drawing, in which the single figure is a partly cross-sectional view through a non-linear resistor in accordance with the invention.

Before proceeding with a detailed description of the non-linear resistors contemplated by the invention, their construction will be described with reference to the aforesaid figure of the drawing, wherein reference character **10** designates, as a whole, a non-linear resistor having, as its active element, a sintered wafer **1** of electrically conductive ceramic material according to the present invention.

Sintered wafer **1** is prepared in a manner hereinafter set forth, and is provided with a pair of electrodes **2** and **3** having specified compositions and applied in a suitable manner, hereinafter set forth, on two opposite surfaces of the wafer.

One of said pair of electrodes, for example, the electrode **2** is a silver electrode in non-ohmic contact with the wafer **1**, and the other electrode **3** is in ohmic contact with the wafer **1** in accordance with the invention.

The wafer **1** is a sintered plate having any one of a number of various shapes such as circular, square, rectangular, etc. Wire leads **5** and **6** are attached conductively to the electrodes **2** and **3**, respectively, by a connection means **4**, such as solder or the like.

According to the present invention, sintered wafer **1** consists essentially of, as an active ingredient, zinc oxide (ZnO). It is preferable that said zinc oxide have incorporated therein a proportion of 0.05 to 10.0 mol percent of at least one oxide selected from the group consisting of aluminum oxide (Al_2O_3). iron oxide (Fe_2O_3), bismuth oxide (Bi_2O_3), magnesium oxide (MgO), calcium oxide (CaO), nickel oxide (NiO), cobalt oxide (CoO), niobium oxide (Nb_2O_5), tantalum oxide (Ta_2O_5), zirconium oxide (ZrO_2), tungsten oxide (WO_3), cadmium oxide (CdO), and chromium oxide (Cr_2O_3).

It has been discovered according to the invention that sintered wafer **1** will be in non-ohmic contact with said silver electrode **2** when said silver electrode is prepared by applying silver paint to one surface of said wafer and firing the thus coated wafer at 100° C. to 850° C. in an oxidizing atmosphere, such as air or oxygen.

Table 1 shows operable and optimal compositions of silver electrode **2** after heating for curing in order to produce the novel non-linear resistors in accordance with the invention.

It is important for achieving a non-ohmic contact that said silver electrode be prepared by firing, at a temperature of 100 to 850° C. in an oxidizing atmosphere such as air and oxygen, a silver paint which is applied to the surface of said sintered wafer and which has a composition similar with respect to the solid ingredients to that of the fired silver electrode.

The other electrode, in ohmic contact with the wafer, is formed by vacuum-evaporating a metal selected from the group consisting of aluminum, zinc, tin and indium, in accordance with the invention.

Another method for making said electrode which is in ohmic contact according to the invention is to plate electro-chemically a metal selected from the group consisting of silver, copper, nickel, zinc, and tin.

A further operable electrode which is in ohmic contact can be formed by a spray metalized film of a metal selected from the group consisting of copper, tin, zinc and aluminum.

Composition of silver electrode (wt. percent):
- PbO—1.2–17
- SiO_2—0.1–6.0
- B_2O_3—0.06–6.0
- Bi_2O_3—0–2.0
- CdO—0–2.0
- CuO—0—2.0

Since the non-linearity of the novel resistors can be attributed to the non-ohmic contact between said sintered wafer **1** and said silver electrode **2**, it is necessary for obtaining a desirable C-value and n-value to control the compositions of the sintered wafer **1** and the silver electrode **2**.

It is necessary for achieving a low value of C for the resultant non-linear resistors that the sintered wafer have an electrical resistivity less than 10 ohm-cm., said electrical resistivity being measured by a four point method in a per se conventional way.

The sintered body **1** can be prepared by a per se well known ceramic technique. The starting materials having the compositions according to the invention are mixed in a wet mill so as to produce homogeneous mixtures. The mixtures are dried and pressed in a mold into desired shapes at a pressure of from 100 kg./cm.^{2} to 1000 kg./cm.^{2}. The pressed bodies are sintered in air at 1250° C. to 1450° C. for 1 to 3 hours, and then furnace cooled to room temperature (from about 15° to about 30° C.). The pressed bodies are preferably sintered in a non-oxidizing atmosphere such as nitrogen or argon when it is desired to reduce the electrical resistivity. The electrical resistivity also can be reduced by air quenching from the sintering temperature to room temperature even when the pressed bodies are fired in air.

TABLE I

Operable composition of electrode, wt. percent (Ag)	Optimal composition of electrode (wt. percent)						
	Ag	PbO	SiO_2	B_2O_3	Bi_2O_3	CdO	CuO
00	70–99.5	0.25–27	0.02–15	0.01–15	0–6.0	0–6.0	0–6.0

It has been discovered according to the invention that a sintered wafer of zinc oxide of the aforesaid composition has an excellent non-linearity as a non-linear resistor and a high stability with respect to humidity, temperature, and electric load when it is provided, at one surface thereof, with a silver electrode which is in non-ohmic contact therewith and has the aforesaid composition, and at the other surface thereof, with another electrode in ohmic contact therewith, as described hereinbefore. Such a non-linear resistor is a non-symmetrical type and can be connected at said silver electrode to a positive terminal of a DC source and, at said electrode in ohmic contact, to a negative terminal of DC source. A great feature of the non-linear resistor of the non-symmetrical type according to the invention is the combination of a high n-value and a low C-value, lower than 1.0 at a given current of 100 ma.

Table 2 shows optimal compositions for the combination of the sintered wafer **1** and the silver electrode in accordance with the invention. A non-linear resistor with such optimal compositions has a C-value lower than 0.8 at a given current of 100 ma., an n-value higher than 10 and a high stability with respect to temperature, humidity and electric load, when it is provided with the other electrode **3** consisting of any one of the aforesaid operable electrodes in ohmic contact therewith in accordance with the invention.

TABLE 2.—OPTIMAL COMPOSITION OF SINTERED WAFER AND SILVER ELECTRODE

Composition of sintered wafer (mol percent):
- ZnO—100–98
- Fe_2O_3—0–2.0

The mixtures can, if desired, be preliminarily calcined at 700 to 1000° C. and pulverized for easy fabrication in the subsequent pressing step. The mixture to be pressed can be admixed with a suitable binder such as water, polyvinyl alcohol, etc.

The sintered bodies in wafer form are coated on one surface thereof by a silver electrode paint in a per se conventional manner such as by a spray method, screen printing method or brushing method. It is necessary that the silver electrode paint have a solid ingredient composition as defined in Tables 1 and 2 after it is fired at 100° C. to 850° C. in air. Solid ingredients having compositions defined in Tables 1 and 2 can be prepared in a per se conventional manner by mixing commercially available powders with organic resin such as epoxy, vinyl and phenol resin in an organic solvent such as butyl acetate, toluene or the like so as to produce silver electrode paints.

The silver powder may be in the form of metallic silver, or in the form of silver carbonate or silver oxide, or in any other form which during firing at the temperatures employed will be converted to metallic silver. Therefore, the term "silver" as used throughout this specification and the claims appended hereto in connection with the silver composition before it is fired, is meant to include silver in any form which during firing will be converted to metallic silver. The viscosity of the resultant silver electrode paints can be controlled by the amounts of resin and solvent. The particle sizes of the solid ingredients also are required to be controlled so as to be in the range of 0.1μ to 5μ.

A sintered wafer, after being provided on one surface thereof with said silver electrode, is provided, on the other surface thereof, with an electrode in ohmic contact by vacuum evaporation, electrochemical plating or spray metallizing in a per se well known manner.

Lead wires can be applied to the silver electrode and the electrode in ohmic contact in a per se conventional manner by using conventional solder having a low melting point. It is convenient to employ a conductive adhesive comprising silver powder and resin in an organic solvent for connecting the lead wires to the silver electrode and the ohmic contact electrode.

Non-linear resistors according to this invention have a high stability with respect to temperature and in a load life test, which is carried out at 70° C. at rated power for 500 hours. The *n*-value and C-value do not change significantly after being subjected to heating cycles and a load life test. It is preferable for achieving a high stability with respect to humidity that the resultant non-linear resistors be embedded in a humidity proof resin such as epoxy resin and phenol resin in a per se well known manner.

According to the invention, it has been discovered that the curing method for the applied silver electrode paint has a great effect on the *n*-value of the resultant non-linear resistors. The *n*-value will not be optimal when the applied silver electrode paint is heated in a non-oxidizing atmosphere such as nitrogen or hydrogen for curing. It is necessary for obtaining a high *n*-value that the applied silver electrode paint be cured by heating in an oxidizing atmosphere such as air or oxygen.

A silver electrode prepared by any method other than by silver painting results in a resistor having a poor *n*-value. For example, the sintered body does not act as a non-linear resistor when it is provided with a silver electrode by electroless plating or electrolytic plating in a conventional manner. A silver electrode prepared by vacuum evaporation or chemical deposition results in a resistor having an *n*-value less than 3.

The following examples are given as illustrative of the presently-preferred method of proceeding according to the present invention; however, it is not intended that the scope of said invention be limited to the specific examples.

TABLE 3

Starting materials (mol percent)		Electric characteristic of resultant resistors	
ZnO	Additives	C[1]	*n*
100	0	0.75	16.0
99.5	0.5 Al_2O_3	0.50	9.2
98.5	1.5 Al_2O_3	0.62	8.0
99.95	0.05 Fe_2O_3	0.70	12.0
99.9	0.1 Fe_2O_3	0.66	12.8
99.8	0.2 Fe_2O_3	0.64	13.5
99.5	0.5 Fe_2O_3	0.62	14.0
99.0	1.0 Fe_2O_3	0.65	13.0
98.0	2.0 Fe_2O_3	0.67	12.3

[1] At a given current of 100 ma.

EXAMPLE 1

Starting materials according to Table 3 were mixed in a wet mill for 5 hours.

The mixtures were dried and pressed in molds into discs of 13 mm. diameter and 2.0 mm. thick at a pressure of 340 kg./cm.^{2}.

The pressed bodies were sintered in air at 1350° C. for 1 hour, and then quenched to room temperature (about 15° to about 30° C.). The resulting sintered discs were 10 mm. in diameter and 1.5 mm. thick. The sintered discs were coated on one surface thereof with a silver electrode paint by a conventional brushing method. The silver electrode paint employed had the solid ingredient composition according to Table 4 and was prepared by mixing with vinyl resin in amyl acetate. The coated discs were fired at 500° C. for 30 minutes in air. The other surfaces were provided with a spray metalized film of aluminum by a per se well known technique.

Lead wires were attached to the silver electrodes and the aluminum electrodes by means of conductive silver paint. The electric characteristics of the resultant resistors measured in that direction of easy current flow are shown in Table 3.

TABLE 4

Composition of silver electrode wt. percent:

Ag	90
PbO	7.0
SiO_2	2.0
B_2O_3	0.7
CuO	0.3

EXAMPLE 2

Sintered discs each having a composition of 99.5 mol. percent of zinc oxide and 0.5 mol. percent of iron oxide were prepared in the same manner as in Example 1. The sintered discs were 10 mm. in diameter and 1.5 mm. thick. Various silver electrode paints were applied to one surface of the respective sintered discs and the coated discs were fired at 500° C. for 30 minutes in air. The silver electrode paints had solid ingredient compositions as shown in Table 5 and are prepared by mixing 100 parts by weight of said solid ingredient compositions with 1 to 20 parts by weight of epoxy resin in 20 to 40 parts by weight of butyl alcohol. The other surfaces were provided with a nickel electrode by an electroless plating method. The resultant non-linear resistors had desirable C-values and n-values as indicated in Table 5. It will thus be readily understood that the electrode compositions have a great effect on the electrical characteristics of the resultant non-linear resistors.

EXAMPLE 3

The resistors of Example 1 were tested according to the methods used for testing electronic component parts. The load life test was carried out at 70° C. ambient temperature at a 1 watt rating power for 500 hours. The heating cycle test was carried out by repeating 5 times a cycle in which said resistors were kept at 85° C. ambient temperature for 30 minutes, cooled rapidly to −20° C. and then kept at such temperature for 30 minutes. After the heating cycle and load life tests, the C-value and *n*-values did not change more than 1.5% and 3%, respectively.

TABLE 5

Composition of electrode (wt. percent)							The characteristics of the resultant resistors	
Ag	PbO	SiO_2	B_2O_3	Bi_2O_3	CdO	CuO	C[1]	*n*
95	3.5	1.0	0.5				0.64	10.2
95	3.3	0.8	0.3	0.6			0.61	8.2
90	6.2	2.0	0.8	1.0			0.67	10.8
90	6.5	2.0	0.8		0.7		0.67	12.6
90	6.5	2.0	0.8			0.7	0.70	12.5
90	6.5	2.0	0.8		0.4	0.3	0.69	11.5
85	10.0	3.0	1.0	0.3	0.4	0.3	0.73	10.3

[1] At a given current of 100 ma.

What is claimed is:

1. A non-linear resistor comprising a sintered disc of zinc oxide and two electrodes, one applied to each of the opposite surfaces of said sintered disc, one of said two electrodes being a silver electrode in non-ohmic contact with one of said opposite surfaces, and the other of said two electrodes being in ohmic contact with another of said opposite surfaces.

2. A non-linear resistor according to claim **1**, wherein said sintered disc consists essentially of zinc oxide.

3. A non-linear resistor according to claim **1**, wherein said sintered disc consists essentially of 99.95 to 90 mol percent of zinc oxide and 0.05 to 10.0 mol percent of at least one oxide selected from the group consisting of Fe_2O_3, Al_2O_3, Bi_2O_3, MgO, CaO, NiO, CoO, Nb_2O_5, Ta_2O_5, ZrO_2, WO_3, CdO, and Cr_2O_3.

4. A non-linear resistor according to claim **1**, wherein said silver electrode is 100 percent by weight Ag.

5. A non-linear resistor according to claim 1, wherein said silver electrode consists essentially of 0.25 to 27 percent by weight PbO, 0.02 to 15 percent by weight SiO_2, 0.01 to 15 percent by weight B_2O_3, 0 to 6.0 percent by weight Bi_2O_3, 0 to 6.0 percent by weight CdO, 0 to 6.0 percent by weight CuO and the balance silver.

6. A non-linear resistor according to claim 1, wherein said sintered disc consists essentially of 100 to 98.0 mol percent ZnO and 0 to 2.0 mol percent Fe_2O_3, and said silver electrode consists essentially of 1.2 to 17.0 percent by weight PbO, 0.1 to 6.0 percent by weight SiO_2, 0.06 to 6.0 percent by weight B_2O_3, 0 to 2.0 percent by weight Bi_2O_3, 0 to 2.0 percent by weight CdO, 0 to 2.0 percent by weight CuO and the balance silver.

7. A non-linear resistor according to claim 1, wherein said other electrode in ohmic contact consists essentially of an evaporated film of a metal selected from the group consisting of aluminum, zinc, tin and indium.

8. A non-linear resistor according to claim 1, wherein said other electrode in ohmic contact consists essentially of an electrochemically plated film of a metal selected

from the group consisting of silver, copper, nickel, zinc and tin.

9. A non-linear resistor according to claim 1, wherein said other electrode in an ohmic contact consists essentially of a spray metalized film of a metal selected from the group consisting of copper, tin, zinc and aluminum.

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