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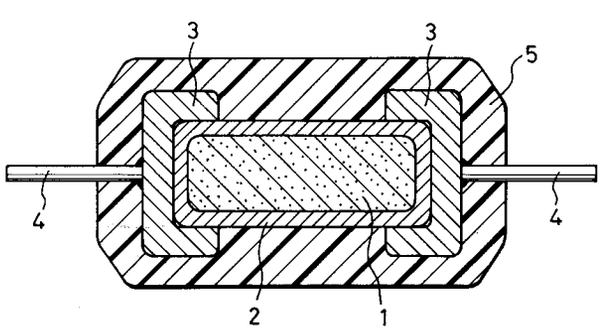
(54) Metal oxide film resistor and method for producing the same.

(57) A metal oxide film resistor comprises mainly zinc oxide and an auxiliary oxide of at least one metal added as an activator for covering a wide range of resistance of from 1 kΩ to 10 MΩ. A method of producing such a metal oxide film resistor comprises the steps of preparing a solution composed of at least a zinc salt, and forming a zinc oxide film (2) on an insulating substrate (1) by supplying a vapor of the solution to the insulating substrate (1) heated to a temperature at which the zinc salt thermally decomposes and by thermally decomposing the zinc salt on the surface of the insulating substrate (1).

FIG.1



EP 0 660 337 A2

BACKGROUND OF THE INVENTION

1. Field of the Invention

The present invention relates to a metal oxide film resistor which has a wide application for configuring circuits in various electric appliances, and a method for producing such metal oxide film resistors.

2. Description of the Related Art

Conventional metal oxide film resistors are generally configured with insulating substrates of rod-type made of mullite or alumina, metal oxide films comprising tin oxide or antimony-doped tin oxide (hereinafter referred to ATO) formed on the surfaces of the substrates, pairs of metal cap terminals press-fitted on both ends of the substrates, lead wires welded to the terminals, and electrically insulating protective films formed on the surfaces of the resistors.

Of these metal oxide film resistors, those comprising a single phase of tin oxide have a very large temperature coefficient of resistance and their conditions for application are extremely limited, and are therefore not practical. For this reason, the ATO has now been put to practical use as the material for the metal oxide film in general.

The method for producing the metal oxide film is generally performed in a chemical process of forming a film such as spraying or chemical vapor deposition (CVD). In these processes, a film of ATO is formed on the surface of the substrate by spraying a vapor of an aqueous solution or an organic solvent solution containing stannic chloride and antimony trichloride to the substrate of rod-type which is placed in a furnace elevated to a temperature of 600 - 800 °C. Thereafter, a pair of metal cap terminals are press-fitted on both ends of the substrate, and a part of the film is cut or grooved in order to adjust the resistance of the film to have a desired value. The metal oxide film resistor is completed by welding a pair of lead wires to the cap terminals, and forming a resin protective coating film on these components.

The metal oxide film resistor using the ATO film has a disadvantage that a specific resistance of the ATO film is relatively low, such as from about 1×10^{-3} to about 1×10^{-2} Ω•cm. Therefore, the film thickness must be made considerably thin for making a resistance value of 100 kΩ or above, as far as using only one method of adjusting the resistance value, that is controlling of the film thickness. However, in fact it is difficult to control the film thickness of the thin film, and therefore to obtain a metal oxide film resistor having a desired resistance value and a stable and uniform quality, presumably because of a large variance or dispersion in its film thickness. Due to the above-mentioned disadvantages in the manufacturing process such as the large variance in its resistance value, it has been difficult to obtain a metal oxide film resistor having a desired resistance value with a stable and uniform quality and a high reliability.

SUMMARY OF THE INVENTION

The present invention is proposed in order to overcome the above-mentioned disadvantages and deficiencies of the prior art, and is intended to provide a metal oxide film resistor having a desired resistance value in a wide range from 1 kΩ to 10 MΩ, and a stable and uniform quality.

It is another object of the present invention to provide a method for producing a metal oxide film resistor having a constant film thickness, and a small variance in its resistance.

The present invention provides a metal oxide film resistor comprising: an insulating substrate, a zinc oxide film formed on the surface of the insulating substrate, and a pair of terminals which are in contact with the zinc oxide film.

In a preferred embodiment of the present invention, the metal oxide film further comprises an oxide of at least one metal selected from the group consisting of aluminum, magnesium, scandium, titanium, vanadium, chromium, manganese, iron, cobalt, nickel, copper, yttrium, zirconium, indium, tin, antimony, lanthanum and cerium, in addition to the zinc oxide. In the following description, any compounds of these metals are referred to as an activator.

The present invention also provides a method for producing a metal oxide film resistor comprising the step of forming a zinc oxide film on a surface of an insulating substrate by thermally decomposing a zinc salt on the surface of the insulating substrate under an atmosphere containing oxygen or in a coexistence with a material capable of supplying oxygen.

In a preferred embodiment of the method for producing a metal oxide film resistor in accordance with the present invention, the zinc salt is thermally decomposed on the surface of the insulating substrate to form a zinc oxide film on the surface of the substrate by supplying a vapor of a solution containing the zinc

salt to the insulating substrate heated to a temperature at which the zinc salt thermally decomposes. The above-mentioned thermal decomposition step can also be performed under an inert gas atmosphere such as nitrogen, not to mention an atmosphere containing oxygen. In the former case, the oxygen for forming the zinc oxide by the thermal decomposition of the zinc salt is supplied from the solution which dissolves the zinc salt.

In another preferred embodiment of the present invention, in order to form the zinc oxide on the insulating substrate, the insulating substrate on which surface a coated film containing the zinc salt has been formed is heated under an atmosphere containing oxygen to a temperature or above at which the zinc salt thermally decomposes.

Another preferred embodiment of the method of the present invention comprises: the steps of,

applying a solution containing at least a zinc salt, an organic compound capable of coordinating to zinc, and an organic solvent capable of dissolving the zinc salt and the organic compound to the insulating substrate to form a coated film containing the zinc salt, and

firing the coated film to form a zinc oxide film under an atmosphere containing oxygen to form the zinc oxide film.

In another embodiment of the present invention, the above-mentioned solution containing the zinc salt further comprises: an inorganic salt or an organic salt of at least one metal selected from the group consisting of aluminum, magnesium, scandium, titanium, vanadium, chromium, manganese, iron, cobalt, nickel, copper, yttrium, zirconium, indium, tin, antimony, lanthanum and cerium, in addition to the zinc salt.

While the novel features of the present invention are set forth particularly in the appended claims, the invention, both as to organization and content, will be better understood and appreciated, along with other objects and features thereof, from the following detailed description taken in conjunction with the attached drawings.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG.1 is a cross-sectional side view showing a schematic configuration of the metal oxide film resistor built in accordance with an embodiment of the present invention.

FIG.2 is a cross-sectional side view showing a schematic configuration of an apparatus for producing the metal oxide film resistor built in accordance with an embodiment of the present invention.

FIG.3 is a cross-sectional side view showing a schematic configuration of an apparatus used for producing the metal oxide film resistor built in accordance with another embodiment of the present invention.

FIG.4 is a diagram showing electric characteristics of metal oxide film resistors built in accordance with the embodiments of the present invention.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

As stated previously, the zinc oxide film of the present invention is produced by applying a solution comprising at least a zinc salt, an organic compound capable of coordinating to zinc and an organic solvent capable of dissolving the zinc salt and the organic compound to form a coated film on the surface of the insulating substrate, and by firing the coated film under an atmosphere containing oxygen.

Any of the zinc salts can be employed as far as it contains a ligand that can be exchanged or substituted with the organic compound capable of coordinating to zinc. In preferred embodiments, zinc nitrate, zinc chloride, zinc sulfate, zinc oxalate and the like are employed as the zinc salt in addition to the exemplified zinc acetate.

The organic compound capable of coordinating to zinc is necessary for giving a solubility in the organic solvent to zinc by partly forming a coordination compound with zinc, and can be exemplified as α- or β-aminoalcohols such as 2-aminoethanol, β-diketones such as acetylacetone, α- or β-ketonic acids and any esters of the ketonic acids.

Any of the organic solvents can be employed as far as it can dissolve the organic compounds and inorganic compounds used in the present invention, and may be exemplified as aromatic hydrocarbons such as toluene and xylene, alcohols such as ethanol and isopropanol, acetic acid esters such as ethyl acetate and butyl acetate, ketones such as acetone and diethylketone, ethers such as tetrahydrofuran, etheralcohols such as methoxyethanol and ethoxyethanol, and the like.

The activator is a metal salt added to the film-forming composition in order to adjust the resistance value and the temperature coefficient of resistance (TCR) of the finished zinc oxide film, and the metal element in the salt can be exemplified as aluminum, magnesium, scandium, titanium, vanadium, chromium,

manganese, iron, cobalt, nickel, copper, yttrium, zirconium, indium, tin, antimony, lanthanum and cerium. These metals are employed as their inorganic salts such as nitrate, chloride, sulfate and fluoride, or their organic salts, for example, a salt of carboxylic acid such as acetic acid salt and 2-ethylhexanoic acid salt, a salt of dicarboxylic acid such as oxalic acid salt, complex salts with acetylacetone, and the like.

In the method of production of the present invention, a solution composed of at least a zinc salt, an organic compound capable of coordinating to zinc, and an organic solvent capable of dissolving the zinc salt and the organic compound, is employed as a composition for forming the metal oxide film. In preparing this composition, it is preferable to reflux the above-mentioned components at a temperature where the organic solvent can be refluxed. This refluxing treatment is performed in order to promote a reaction of the zinc salt or another salt of metal further added as an activator with the organic compound capable of coordinating to zinc, and is not necessarily indispensable for the preparation of the solution. When an activator having a very low solubility at room temperature is employed, the refluxing treatment is an effective means for the preparation of the solution.

The organic compound capable of coordinating to zinc has a function of suppressing possible hydrolysis of the zinc salt by forming a coordination compound with zinc. During a thermal decomposition process, a part of the organic compound capable of coordinating to zinc, which has failed to form a coordination compound with zinc and remains after an evaporation of the organic solvent, functions as an auxiliary solvent for the above-mentioned zinc salt until the thermal decomposition of the above-mentioned zinc salt is actually completed, and creates a situation wherein a deposition of the above-mentioned zinc salt takes place simultaneous with its thermal decomposition. Owing to the presence of the organic compound capable of coordinating to zinc in the solution, it is possible to obtain a very fine and dense film.

Further, when, as an activator, another metal M salt is added to the solution in order to cause the other metal to be included in the finished zinc oxide film, a deposition and a thermal decomposition of both of the above-mentioned zinc salt and the activator take place simultaneously. Since a metal oxide film having a very small deviation in its composition can be produced by the above-mentioned function of the organic compound capable of coordinating to zinc, it is possible to produce a metal oxide film resistor having a very small variance in its resistance value in a stable operation.

As previously described, since the organic compound capable of coordinating to zinc considerably participates in the thermal decomposition process of the zinc salt, the characteristics of the obtained film are greatly influenced by the property (for instance, boiling point) of the compound. Therefore, an adequate selection of the species of organic compound is important.

As a method for applying the metal oxide film-forming composition prepared in the above-mentioned manner to the surface of the substrate, employed are a dip-coating process, a spraying method, a dispenser method and the like.

The substrate employed in the present invention should have an electrically insulating property at least on its surface, and is preferably exemplified as ceramic materials such as mullite, alumina, forsterite, steatite and cordierite.

The coated film of the composition for forming the metal oxide film is dried, and then fired to form the metal oxide film comprising zinc oxide or the one comprising zinc oxide as its principal component and the other oxide(s) of the metal M. The temperature for performing the firing step is above a temperature at which the composition for forming the metal oxide film is thermally decomposed and is below a temperature at which the substrate deforms, and is preferably in a range from 400 °C to 900 °C. The atmosphere under which the above-mentioned firing step is performed is air or an atmosphere including oxygen. The thickness of the metal oxide film formed in this manner is usually in a range from several tens nm to several hundreds nm.

The previously described prior art ATO films have a disadvantage that they have a large deviation or scatter in their resistance value because they are produced by a spraying process or the like that has unstable film forming conditions and they contain antimony which is thermally unstable.

In contrast to this, it is apparent from the foregoing description that the above-mentioned method in accordance with the present invention can overcome the mentioned disadvantage.

A more preferable method for producing the zinc oxide film of the present invention is a method to form the zinc oxide film on the surface of the insulating substrate by supplying a vapor of a solution containing the zinc salt to the insulating substrate heated to a temperature at or above which the zinc salt can be thermally decomposed and by decomposing the zinc salt on the surface of the insulating substrate to form a zinc oxide film on the surface of the substrate.

In this case, the above-mentioned zinc salt solution can further contain the metal salt(s) of the above-mentioned activator.

Any of the solvents used for preparing the solution containing the above-mentioned zinc salt and the above-mentioned metal salt(s) can be employed as far as it can dissolve the above-mentioned zinc salt and other metal salt(s). They may be exemplified as alcohols such as ethanol and isopropanol, acetic acid esters such as ethyl acetate and butyl acetate, ketones such as acetone and diethylketone, etheralcohols such as methoxyethanol and ethoxyethanol, and the like. The most preferable solvent is water. In order to promote the dissolution of these salts, acid such as hydrochloric acid, sulfuric acid and nitric acid or ammonia may be added to the solvent.

The temperature of heating the insulating substrate, whereto the vapor of the solution containing the zinc salt is supplied to be thermally decomposed in situ, must be lower than the melting point of the obtained metal oxide and also lower than the temperature at which the substrate deforms. The higher the temperature is, the more preferable the quality of the obtained metal oxide film becomes. A temperature ranging from 400 °C to 900 °C is generally preferable for this purpose. The atmosphere under which the above-mentioned decomposition step is performed is an inert gas atmosphere such as nitrogen or argon in addition to air or an atmosphere including oxygen. The thickness of the metal oxide film formed in this manner is usually in a range from several tens nm to several thousands nm.

For the oxide film obtained by either of the above-mentioned methods, it is preferable to further subject it to a heat-treatment under an inert gas atmosphere such as nitrogen or argon, a reducing gas atmosphere such as hydrogen or a mixed gas atmosphere of the inert gas and hydrogen. By this heat-treatment, a desorption of oxygen which has been chemically adsorbed on the surface of the oxide film and a formation of vacant hole of oxygen in the crystals of the zinc oxide take place. A resistor film having a smaller variance in the resistance value is obtained by this treatment.

The atmospheric gas under which the heat-treatment is performed is preferably a nitrogen gas atmosphere or a mixed gas atmosphere of nitrogen and steam from the practical point of view.

The resistance value of the metal oxide film after the formation of the metal oxide film becomes constant within several hours; in the metal oxide film after the above-mentioned heat-treatment under an insert gas or reducing gas atmosphere, however, it takes several days until the resistance value becomes constant. It is believed that the behavior of the metal oxide film of varied resistance value is attributable to oxygen gas which has been adsorbed on the film during the formation of the metal oxide film. By this heat-treatment under an inert gas or reducing gas atmosphere, the oxygen gas which has been adsorbed during the formation of the metal oxide film desorbs therefrom and releases or emits conductive electrons. In this heat-treatment, since only a thermodynamically stable amount of oxygen is still left to be adsorbed, the variance or scatter in the resistance value attributable to the variance in the amount of the adsorbed oxygen decreases.

Incidentally, zinc oxide is a semi-conductor which has a large band gap of 3 eV or larger, and also a conductive material which has a high carrier (conductive electron) concentration. Therefore, by the above-mentioned heat-treatment under the inert gas or the reducing gas atmosphere, the carrier concentration of the zinc oxide increases and the resistance value decreases by the amount of the conductive electrons released or emitted as a result of the desorption of the oxygen gas which has been adsorbed during the formation of the metal oxide film. And, it is believed that since the amount of the conductive electrons in the conduction band becomes very large, the electrons in the lower band (valence band) are hardly excited to the conduction band even with the increase in the temperature. On the contrary, the resistance value rather increases by a scattering of the conductive electrons induced by a lattice vibration, and thus the metal oxide film after the above-mentioned heat-treatment under the inert gas or reducing gas atmosphere demonstrates a positive temperature coefficient of resistance which is analogous to a metal.

As mentioned in the foregoing, if the temperature during the heat-treatment under the inert gas or reducing gas atmosphere is too low, the adsorbed oxygen is hardly desorbed. On the contrary, if the temperature during the heat-treatment under the inert gas or reducing gas atmosphere is too high, the metal oxide film demonstrates a positive and large temperature coefficient of resistance, because the metal oxide film is reduced during the heat-treatment and thus a precipitation of a metal takes place. The degree of reduction may differ from each other depending on the species of the inert gas or the reducing gas, and the upper limit of the heat-treatment temperature falls if a gas is of high reducing ability. Preferably, this heat-treatment is performed at a temperature ranging from 300 °C to 700 °C.

The specific resistance of single phase zinc oxide which constitutes the resistor element of the metal oxide film resistor of the present invention is in a range from about $1 \times 10^{-2}\Omega \cdot cm$ to about $1 \times 10^{2}\Omega \cdot cm$ depending on the amount of oxygen defects present in the oxide film. However, by adequately adjusting the species and the amount of other metal element to be added to the zinc oxide film, it is possible to obtain a zinc oxide film that has a resistance value in a wide range. A film composed of zinc oxide including other metal element can have a specific resistance in a range from about $5 \times 10^{-3}\Omega \cdot cm$ to about $1 \times 10^{3}\Omega \cdot cm$.

Thus, it is possible to obtain a zinc oxide that has a resistance value in a very wide range of a relatively high region of the resistance in comparison with the ATO film of a specific resistance in a narrow range from about $1 \times 10^{-3}\Omega \cdot cm$ to about $1 \times 10^{-2}\Omega \cdot cm$.

It is believed that each of these various metal elements added to the zinc oxide forms a solid solution or a complex oxide with the zinc oxide, or alternatively, becomes a metal oxide, thereby creating a state wherein it is mixed with zinc oxide.

This belief is illustrated in further detail as follows. The metal oxide film in accordance with the present invention can be considered to be in a state wherein the following three local states are mixed:

1. A state wherein the oxide of various metals other than zinc is in a solid solution with the zinc oxide.
2. A state wherein the above-mentioned oxide of various metals forms a compound with the zinc oxide.
3. A state wherein both of the above-mentioned oxide of various metals and the zinc oxide exist discretely without forming a solid solution and/or a compound.

In a case wherein the amount of the metal oxide of various metals is smaller than the solubility limit, the metal oxide is completely dissolved in the zinc oxide in a solid state, but the respective metal oxides may differ from each other with respect to their solubility. And the zinc oxide doped with the metal oxide of various metals exists in a single phase. In a case wherein the amount of the metal oxide of various metals is larger than the solubility limit, all of the metal oxide is not completely dissolved in the zinc oxide in a solid state, and a part of the metal oxide is precipitated in the grain boundaries. And the precipitated metal oxide exists in a dispersed state in a matrix of zinc oxide doped with the metal oxide. Some metal oxide reacts with the zinc oxide to form a compound of the spinel form such as ZnM_2O_4 or $ZnMO_3$ type.

The following examples and comparative examples are given for the purpose of further illustrating the present invention with reference to the attached drawings, but are in no way to be taken as limiting.

Structure of the metal oxide film resistor

FIG.1 shows a schematic configuration of the metal oxide film resistor produced in accordance with an embodiment of the present invention.

As shown by FIG.1, a metal oxide film 2 is formed on a surface of an insulating substrate 1 in the above-mentioned manner. A pair of cap terminals 3 made of stainless steel plated with tin were press-fitted on both ends of the substrate 1 having been formed with the above-mentioned metal oxide film 2 and a pair of copper lead wires 4 plated with tin were welded to the cap terminals 3. As the cap terminals 3, any terminals may be used as far as they can ohmically connected to the metal oxide film 2, and as the lead wires 4, any lead wires may be used as far as they can be ohmically connected to the cap terminals 3.

Further, the surface of the above-mentioned metal oxide film 2 was coated with a protective film 5 made of a thermosetting resin. As shown in the example, the protective film 5 also covers the cap terminals 3. Any material may be used as the protective film 5 as far as it has an electrically insulating property and a humidity-resistant property, and may be the resin itself or the resin containing an inorganic filler. For curing the resin, a radiation of visible light or ultraviolet ray may also be used in place of the application of heat.

Apparatus for coating the metal oxide film

FIG.2 shows an apparatus for supplying a vapor of a solution containing the zinc salt on the surface of the heated insulating substrate and for forming a metal oxide film thereon.

A reaction tube 11 made of quartz accommodating the insulating substrate 1 on whose surface the metal oxide film is to be formed is fixed to a furnace core tube 12 made also of quartz with a pair of packing rings 13. The furnace core tube 12 inserted in an electric furnace 14 is caused to rotate in the electric furnace 14 by chain 16 which is driven by an electric motor 15 at an appropriate revolving speed.

A material supplying container 18 containing the metal oxide film-forming composition 17 is connected with a gas supplying device 19 through a pipe 20, and with the reaction tube 11 through a pipe 21.

In order to form the metal oxide film on the surface of the insulating substrate by the use of this apparatus, a multiplicity of the substrates 1 is first placed in the reaction tube 11 as shown by the drawing. While the reaction tube 11 is rotated, it is heated by the electric furnace 14 and kept at a temperature or above at which the metal oxide film-forming composition decomposes. In this state, a carrier gas supplied from the gas supplying device 19 is introduced into the material supplying container 18 through the pipe 20 and the vapor of the metal oxide film-forming composition is supplied to the reaction tube 11 through the pipe 21.

The above-mentioned vapor which has been supplied to the reaction tube 11 then decomposes by contacting the substrates and forms the metal oxide films on the surfaces of the substrates. In the above-

mentioned apparatus, as the carrier gas supplied from the gas supplying device 19, air, oxygen, or an inert gas such as nitrogen or argon is used. By appropriately adjusting the flow rate of this carrier gas, the supplying amount of the vapor of the above-mentioned metal oxide film-forming composition is controlled. Further, the supplying amount of the vapor of the above-mentioned metal oxide film-forming composition may alternatively be controlled by heating the material supplying container 18 or by applying an ultrasonic radiation to the container 18.

In the exemplified apparatus, the reaction tube 11 is rotated in order to ensure a uniform contact of the vapor containing the zinc salt with the entire surfaces of the substrates by rolling the substrates and to form the metal oxide films throughout the surfaces of the substrates uniformly. In place of rotating the reaction tube 11, a mechanical vibration may be applied to the reaction tube 11 for the same purpose.

In the apparatus shown by FIG.2, the metal oxide film-forming composition is supplied to the reaction tube 11 by the pressurized carrier gas.

An apparatus shown by FIG.3 is configured by connecting a pressure reducing device 23 to an exhaust side of the reaction tube 11 through a pipe 22 and creates a pressure difference between the spaces inside the pipes 20 and 22. So that the pressure inside the reaction tube 11 is reduced to introduce the carrier gas into the material supplying container 18, and then the vapor of the metal oxide film-forming composition is supplied to the reaction tube 11. In this apparatus, by appropriately adjusting the gas exhausting amount of the pressure reducing device 23, the supplying amount of the vapor of the above-mentioned metal oxide film-forming composition may be controlled. Further, the supplying amount of the vapor of the above-mentioned metal oxide film-forming composition may alternatively be controlled by heating the material supplying container 18 or by applying an ultrasonic radiation to the container 18.

In the apparatuses shown in FIG.2 and FIG.3, the connections of the reaction tube 11 with the pipe 21 are configured with gas-tight sealing joints so that any gas or vapor should not be leaked even with the rotation of the reaction tube 11. In the apparatus shown in FIG.3, the connection of the reaction tube 11 with the pipe 22 is configured in the same manner.

EXAMPLE 1

Synthesis of Metal Oxide Film-Forming Composition

To 66 g of zinc acetate $Zn(CH_3CO_2)_2 \cdot 2H_2O$ weighed and placed in a conical flask of 1 liter volume, added were 100 g of 2-aminoethanol $H_2NC_2H_5OH$, and mixed in room temperature to dissolve. To each portion of the solution thus obtained, added were an acetylacetone complex salt of each of various metals M and methanol weighed in such a manner that a value represented by the formula M/(Zn + M) and converted in terms of mole number of the metals is 0.05 to prepare the metal oxide film-forming compositions.

Coating of Substrate with the Composition

Next, a surface of a substrate of a cylindrical rod was coated with each of the metal oxide film-forming compositions prepared in the above-mentioned manner by means of dip-coating. The substrate was a cylindrical rod made of a ceramic containing 92 wt% of alumina, having a diameter of 2 mm and a length of 10 mm.

After the coated film of the above-mentioned metal oxide film-forming composition was dried at 60 °C for 5 minutes, it was fired in the air at 800 °C for 10 minutes to form a metal oxide film consisting mainly of zinc oxide. The thickness of the film thus produced is about 50 nm.

Assembly of Resistor

A pair of cap terminals 3 were press-fitted on both ends of the substrate 1 having been formed with the above-mentioned metal oxide film 2, and a pair of lead wires 4 were welded to the cap terminals 3.

Next, the surface of the above-mentioned metal oxide film 2 was coated with a paste of a thermosetting resin, dried and then cured by heating it at 150 °C for 10 minutes to form an electrically insulating protective film 5 for completing the metal oxide film resistor of the present invention as shown by FIG.1.

The characteristics of the metal oxide film resistors produced with the respective compositions are summarized in Table 1 below.

Table 1

Metal M	Resistance value(kΩ)
None	1,200
Al	5.0
Mg	31,000
Sc	44.0
Ti	14.0
V	520
Cr	3,500
Mn	57.0
Fe	1,600
Co	14,000
Ni	26,000
Cu	51,000
Y	12.0
Zr	72.0
In	3.0
Sn	9.0
Sb	37.0
La	23.0
Ce	300

EXAMPLE 2

In a manner similar to that in Example 1 except for the use of zinc chloride $ZnCl_2 \cdot 6H_2O$ as the zinc salt and the non-use of any activator, another metal oxide film resistor was prepared.

EXAMPLE 3

In a manner similar to that in Example 2 except for the use of $CH_3COCH_2COCH_3$ as the organic compound capable of coordinating to zinc, another metal oxide film resistor was prepared.

EXAMPLE 4

In a manner similar to that in Example 1 except for the use of aluminum nitrate $Al(NO_3)_3 \cdot 9H_2O$ as the activator in an amount wherein a value represented by the formula Al/(Zn + Al) and converted in terms of mole number of the metals is 0.05, another metal oxide film resistor was prepared.

COMPARATIVE EXAMPLE 1

A metal oxide film-forming composition was prepared by mixing stannic chloride $SnCl_4 \cdot 5H_2O$, antimony trichloride $SbCl_3$ and methanol in a proportion of 100 g, 6.4 g and 10 ml, respectively. This composition was heated at 110 °C to be converted into a state of smoke, and the generated smoke was blown onto a substrate rod kept at 650 °C to form a metal oxide film consisting of the ATO. A pair of cap terminals were press-fitted on both ends of the substrate rod having been formed with the above-mentioned ATO film, and then a pair of lead wires were welded to the cap terminals. Finally, the surface of the above-mentioned ATO film was coated with an electrically insulating protective film for completing the metal oxide film resistor.

The characteristics of the resistors of Examples 2 - 4 and Comparative Example 1 are compared on Table 2 below.

Table 2

	Resistance value (kΩ)
Example 2	1,400
Example 3	1,450
Example 4	6.0
Comparative Example 1	0.15

EXAMPLE 5

Synthesis of Metal Oxide Film-Forming Composition

In a conical flask of 1 liter volume, 3.4 g of zinc chloride $ZnCl_2$, and either of aluminum chloride $AlCl_3$ or indium chloride $InCl_3 \cdot 3H_2O$ in an amount wherein a value represented by the formula M/(Zn + M) and converted in terms of mole number of the metals is 0 - 0.15 were weighed and placed, and 500 ml of deionized water were added thereto. To this mixture, concentrated hydrochloric acid was further added to adjust pH of the solution of the mixture to 4 or lower, thereby completely dissolving the zinc chloride and the aluminum chloride or indium chloride to prepare the metal oxide film-forming composition. In this case, the pH of the solution may be of any value as far as the zinc chloride and the activator such as aluminum chloride or indium chloride can be dissolved. In a case of an aqueous solution, its pH is preferably 4 or lower.

Coating of Substrate with the Composition

An apparatus shown by FIG.2 was used for coating substrates of a cylindrical rod made of a ceramic containing 92 wt% of alumina (diameter: 3mm, length: 14 mm). The substrate rods were placed in a reaction tube 11 and the above-mentioned metal oxide film-forming composition was placed in a material supplying container 18, respectively. The temperature of the material supplying container 18 was kept at room temperature and a mist of the metal oxide film-forming composition was supplied through bubbling. Air was used as a carrier gas, and the flow rate of the gas was kept at 1 liter/minute and the substrate rods were heated up to 800 °C.

The substrate rods in the reaction tube 11 were kept at 800 °C for 60 minutes, and then 50 g of the above-mentioned metal oxide film-forming composition were supplied to the reaction tube 11 for the following 40 minutes to form the metal oxide film. Thereafter, the substrate rods were kept still at 800 °C for the additional 60 minutes. The thickness of the film thus formed was about 3000 nm.

Next, the coated substrate rods were heat-treated under a nitrogen atmosphere at 650 °C for 5 hours. Thereafter, a pair of cap terminals as well as lead wires were attached to each of the substrate rods, and a protective film consisting of a thermosetting resin was formed on these components in a manner similar to that in Example 1.

The electric characteristics of the obtained metal oxide film resistors are shown by a diagram in FIG.4. The diagram illustrates relationships between the resistance values as well as the temperature coefficients of resistance and the values M/(Zn + M) in a metal oxide film of a resistor configured with a zinc oxide film also containing oxide of aluminum or indium.

In FIG.4, the resistance values of the resistors using Al as M and the temperature coefficients of resistance are represented by R_{Al} and TCR_{Al}, while the resistance values of the resistors using In as M and the temperature coefficients of resistance are represented by R_{In} and TCR_{In}, respectively. Further, the temperature coefficients of resistance (TCR) are derived from the values measured at 25 °C and at 125 °C.

EXAMPLE 6

Synthesis of Metal Oxide Film-Forming Composition

In a conical flask of 1 liter volume, 12.6 g of zinc chloride $ZnCl_2 \cdot 6H_2O$, and each of the other chlorides of various metals M in an amount wherein a value represented by the formula M/(Zn + M) and converted in terms of mole number of the metals is 0.02 were weighed and placed, and 100 ml of deionized water were added thereto to dissolve the chlorides. In this manner, each of the metal oxide film-forming compositions

was synthesized.

Coating of Substrate with the Composition

The apparatus shown by FIG.2 was used for coating each of the substrate rods with a metal oxide film with a thickness of about 1000 nm consisting mainly of zinc oxide under the same conditions as those in Example 5.

Without subjecting the coated substrate rods to the heat-treatment under nitrogen atmosphere as in Example 5, they were provided with the terminal caps and lead wires as well as the protective films to complete the metal oxide film resistors. The resistance values of the resistors having the zinc oxide films containing the added metals M are summarized in Table 3 below.

Table 3

Metal M	Resistance value(kΩ)
None	6,200
Al	50.0
Mg	12,000
Sc	84.0
Ti	150
V	2,400
Cr	800
Mn	470
Fe	260
Co	8,800
Ni	9,600
Cu	21,000
Y	120
Zr	720
In	30.0
Sn	93.0
Sb	220
La	81.0
Ce	230

EXAMPLE 7

Under the same conditions as in Example 6 except for the use of zinc acetate $Zn(CH_3COO)_2 \cdot 2H_2O$ as the zinc salt and the non-use of any activator, another metal oxide film resistor was prepared.

EXAMPLE 8

Under the same conditions as in Example 6 except for the use of aluminum acetylacetonate $Al(CH_3COCH_2COCH_3)_3$ as the activator, another metal oxide film resistor was prepared.

EXAMPLE 9

Under the same conditions as in Example 6 except for the use of nitrogen as the carrier gas, another metal oxide film resistor was prepared.

EXAMPLE 10

Under the same conditions as in Example 6 except for the use of an apparatus shown by FIG.3 and the setting of the pressure-reducing device so as to make the flow rate of the carrier gas 1 liter/minute, another metal oxide film resistor was prepared.

COMPARATIVE EXAMPLE 2

A metal oxide film resistor was prepared in a manner similar to that in Comparative Example 1, except for the use of a substrate of cylindrical rod made of a ceramic containing 92 wt% of alumina (diameter: 3 mm, length: 14 mm).

The resistance values of the resistors of the foregoing Examples 7 - 10 as well as Comparative Example 2 are summarized in Table 4 below.

Table 4

	Resistance value (kΩ)
Example 7	6,400
Example 8	52
Example 9	1.5
Example 10	0.95
Comparative Example 2	0.15

Although the present invention has been described in terms of the presently preferred embodiments, it is to be understood that such disclosures are not to be interpreted as limiting. Various alterations and modifications will no doubt become apparent to those skilled in the art to which the present invention pertains, after having read the above disclosure. Accordingly, it is intended that the appended claims be interpreted as covering all alterations and modifications as fall within the true spirit and scope of the invention.

Claims

1. A metal oxide film resistor comprising: an insulating substrate (1), a zinc oxide film (2) formed on the surface of said insulating substrate (1), and a pair of terminals (3) which are in contact with said zinc oxide film (2).

2. A metal oxide film resistor in accordance with claim 1, wherein said zinc oxide film (2) further comprises an oxide of at least one metal selected from the group consisting of aluminum, magnesium, scandium, titanium, vanadium, chromium, manganese, iron, cobalt, nickel, copper, yttrium, zirconium, indium, tin, antimony, lanthanum and cerium.

3. A method for producing a metal oxide film resistor comprising the step of forming a zinc oxide film (2) on a surface of an insulating substrate (1) by thermally decomposing a zinc salt on the surface of the insulating substrate (1) under an atmosphere containing oxygen or in a coexistence with a material capable of supplying oxygen.

4. A method for producing a metal oxide film resistor comprising the steps of:
preparing a solution composed of at least a zinc salt, and
forming a zinc oxide film (2) on an insulating substrate (1) by supplying a vapor of said solution to said insulating substrate (1) heated to a temperature at which said zinc salt thermally decomposes and by thermally decomposing said zinc salt on the surface of said insulating substrate (1).

5. The method for producing a metal oxide film resistor in accordance with claim 4, wherein said solution further comprises an inorganic or organic salt of at least one metal selected from the group consisting of aluminum, magnesium, scandium, titanium, vanadium, chromium, manganese, iron, cobalt, nickel, copper, yttrium, zirconium, indium, tin, antimony, lanthanum and cerium.

6. The method for producing a metal oxide film resistor in accordance with claim 4 or 5, wherein said solution is an acidic aqueous solution.

7. The method for producing a metal oxide film resistor in accordance with claim 4 or 5, wherein the temperature to which said insulating substrate (1) is heated ranges from 400 °C to 900 °C.

8. A method for producing a metal oxide film resistor comprising the steps of:
preparing a solution composed of at least a zinc salt, an organic compound capable of coordinating to zinc, and an organic solvent capable of dissolving said zinc salt and said organic compound,
applying said solution to an insulating substrate (1) to form a coated film, and
forming a zinc oxide film (2) on the surface of said insulating substrate (1) by firing said coated film in the air or under an atmosphere containing oxygen.

9. The method for producing a metal oxide film resistor in accordance with claim 8, wherein said solution further comprises an inorganic or organic salt of at least one metal selected from the group consisting of aluminum, magnesium, scandium, titanium, vanadium, chromium, manganese, iron, cobalt, nickel, copper, yttrium, zirconium, indium, tin, antimony, lanthanum and cerium.

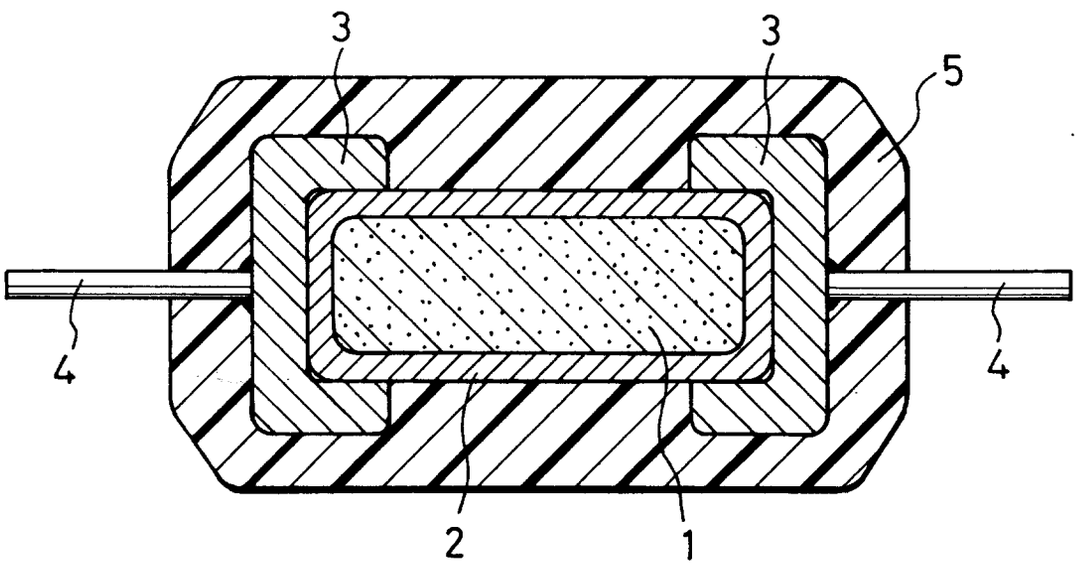
10. The method for producing a metal oxide film resistor in accordance with claim 8 or 9, wherein the temperature of said firing step ranges from 400 °C to 900 °C.

11. The method for producing a metal oxide film resistor in accordance with claim 4, 5, 8 or 9, further comprising the step of heat-treating said metal oxide film (2) under an inert gas atmosphere or a reducing gas atmosphere.

12. The method for producing a metal oxide film resistor in accordance with claim 11, wherein the temperature of said heat-treating step ranges from 300 °C to 700 °C.

13. The method for producing a metal oxide film resistor in accordance with claim 12, wherein the inert gas or reducing gas is at least one member selected from the group consisting of nitrogen, argon and hydrogen.

FIG.1



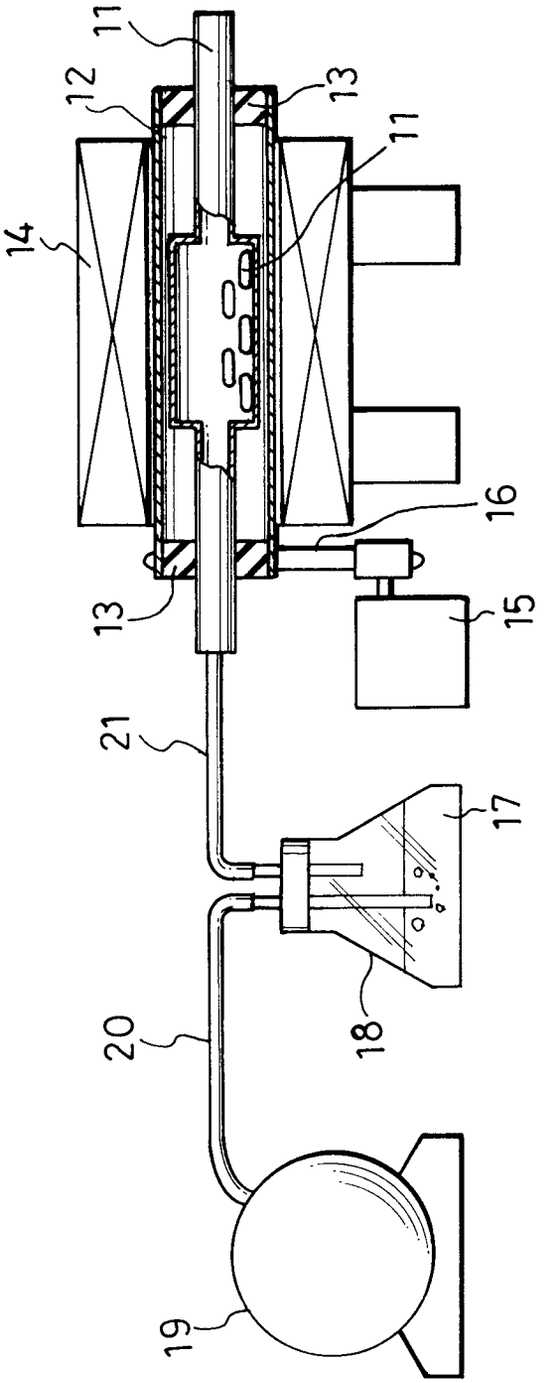


FIG.2

FIG.3

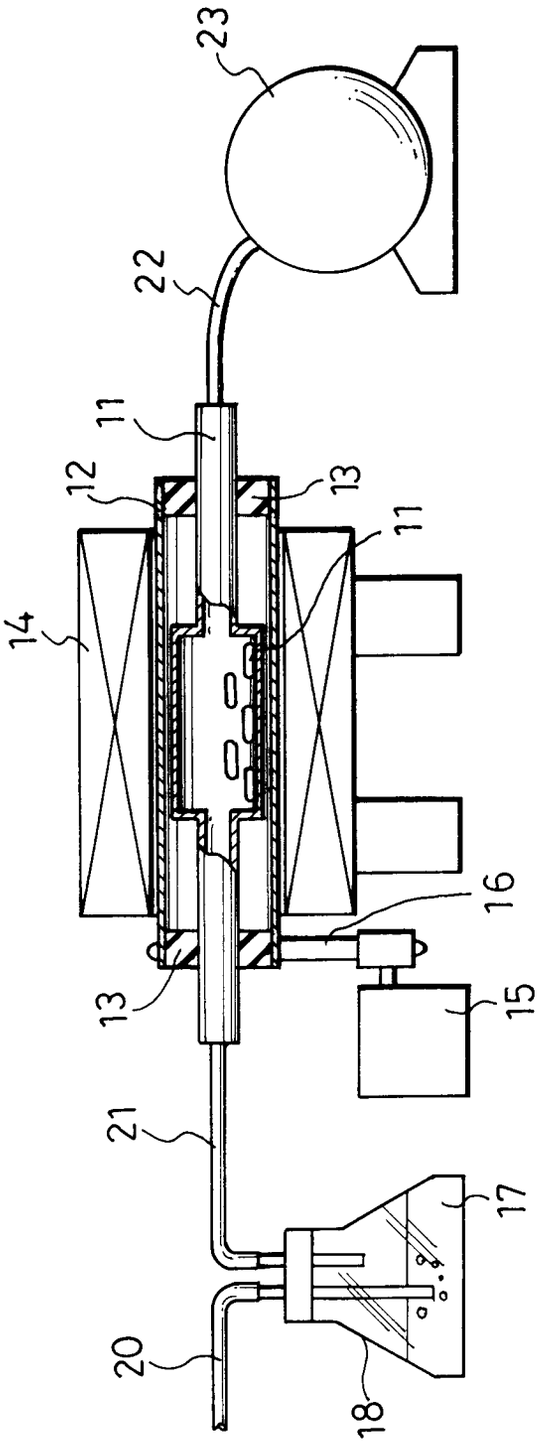
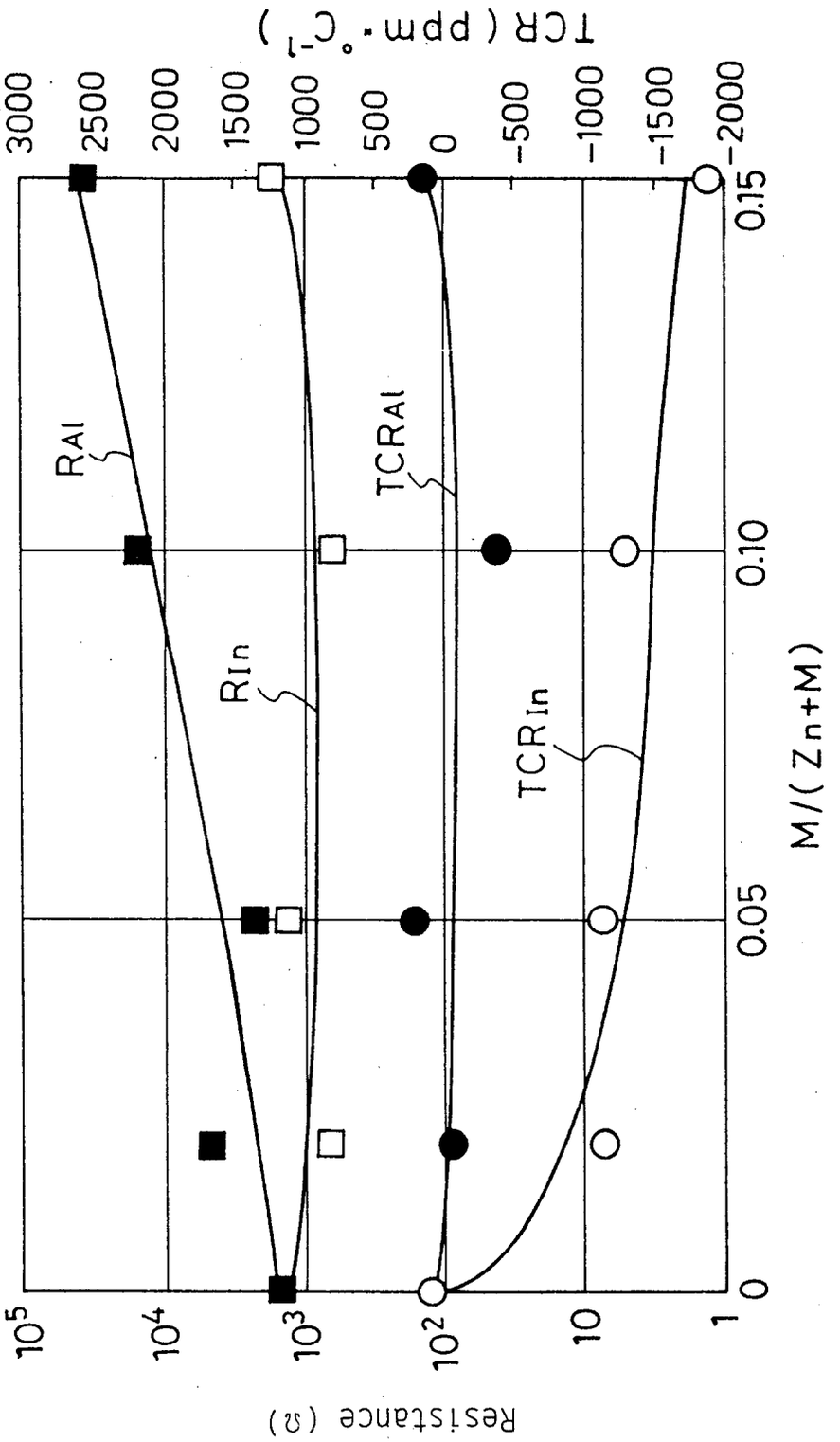


FIG.4


Resistance (Ω)
TCR (ppm·°C⁻¹)
M/(Zn+M)
RAl
RIn
TCRAl
TCRIn
10⁵
10⁴
10³
10²
10
1
3000
2500
2000
1500
1000
500
0
-500
-1000
-1500
-2000
0
0.05
0.10
0.15