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METHOD TO PREPARE OXIDE FILMS

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METHOD TO PREPARE A FILM OF OXIDE

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METHOD TO PREPARE A FILM OF OXIDE

Patent Publication #55-167129

1. Name of the invention

Method to prepare a film of oxide

2. Scope of the patent application

(1) In the production of metal oxide $M_1 M_2 \cdots M_i O_3$ (Note: M1, M2...Mi indicates metal element), the production process starts from the alloy $M_1 M_2 \cdots M_i$ consisting of the oxide of the above described metal. The method to prepare oxide film according to this invention is characterized by the maintenance of said alloy $M_1 M_2 \cdots M_i$ at high temperature in the presence of oxygen and having it oxidized with $M_1 M_2 \cdots M_i O_3$.

(2) The method to prepare a film of oxide according to this invention is characterized by the fact that the metal elements which constitute said metal alloy contain at least one kind of transition element.

(3) The method to prepare a film of oxide according to this invention is characterized by the fact that the metal elements which constitute said metal alloy are thin films of barium and titanium in almost the same mol ratio.

3. Detailed explanation of the invention

This invention concerns the method to prepare a film of oxide which is started from metal alloys of metal oxide metals.

Thermistors have been widely used as temperature sensors as well as sensors to detect radiated heat in the measurement of the wind velocity, flow speed of liquid, degree of vacuous condition and minute flow volume, and thermal transmission rate of gases...etc. The materials used in the thermistors are mainly oxide of transition metals considering the thermal stability of such materials. Since thermistors for the measurement purpose require quick response, small size pead ** type thermistors are generally used. Such thermistors are manufactured according to the following steps.

First, oxide or carbonate of transition metals is mixed according to prescribed ratio, and the mixture is pressure formed and sintered. (At this stage, the sintered material becomes to possess the characteristics of the thermistor.) The sintered material is ground and made into the thermistor powder, which is made into a paste using an aqueous solution containing a few % of dextrin as a binder. The paste is applied over two platinum lines stretched parallel to each other. Then, it is dried and sintered.

In the manufacturing process of the pead ** type thermistor, it is extremely important to strictly manage the

raw material since impurity contained in the raw material will affect the characteristics of the thermistor. As clearly explained in the manufacturing process of the pead ** type thermistor, the size of the grain, viscosity of the paste, the dispersion rate of the thermistor powder within the paste, and the volume of the paste applied on the pead ** are some of the factors which control the characteristics of the element. Generally speaking, all of these factors are difficult to control. Accordingly, fluctuation in the finished product is not rare. Therefore, the relative difference in characteristics among the elements has been the biggest problem.

The objective of this invention is to eliminate the shortcoming described above and to provide the method to prepare a film of oxide by which miniaturized thermistors with the least amount of fluctuation and the highest level of dependability can be manufactured.

The film of oxide by this invention preferably is made from highly pure and evenly formed alloys of a rolled metal sheet, cable material or platinum. These films of oxide are known to make the best use of the thermistor characteristics of the films of oxide. Because it is possible to introduce the technology of micro-manufacturing as far as the alloy films are concerned, it is possible to uniformalize the superior characteristics of the thermistor.

Next, the method to manufacture a film of oxide according

to this invention is explained in the practical applications of this invention using the example of the thermistor.

Practical application #1

A rectangular piece, 2 mm wide and 4 mm long, was cut from a rolled sheet of metal, 0.5 mm in thickness, made of an alloy of nickel and iron which contained 20 weight % of iron. The metal piece was heated to 800 degrees C in the atmosphere for 30 minutes in order to form a dense film of oxide on the surface of the rectangular piece. Next, silver glaze past was applied to the both end of the rectangular piece, and the rectangular piece was baked in order to glaze the past on the rectangular piece. Lead wires were attached to the piece with a soldering iron in order to measure the thermistor characteristics of the piece. The resistance figure at 24 degrees C temperature was 45.7 K Ohm, and the B constant was 4260.

Practical application #2

A cable wire, 1 mm in diameter, made of an alloy of nickel and iron containing 20 weight % of iron was cut to 4 mm length and kept in the atmosphere at 800 degrees C temperature for 30 minutes in order to form a dense film of oxide on its surface. Next, iron glaze past was applied to the both end of the wire, and the cable wire piece was baked in order to glaze the past on the wire piece. Thermistor characteristics of the

wire cable piece were measured according to the same method as the practical application #1. The resistance figure at 24 degrees C was 50.3 K Ohm, and the B constant was 4230.

Practical application #3

An alloy of copper, nickel and manganese containing 60 % of copper, 20 % of nickel and 20 % of manganese was ** on the alumina substrate by electronic beams. The shape of the ** film was rectangular, 3 mm in width and 4 mm in length, and approximately 2 micra in thickness. The piece was oxidized in the atmosphere at 850 degrees C temperature for 15 minutes. Next, ** glaze paste was printed on the both end of the metal piece, and the piece was baked in order to glaze the paste on the piece. Thermistor characteristics of the metal piece was measured according to the same method as the practical application #1. The resistance figure at 20 degrees C was 5.5 ** M Ohm, and the B constant was 2500.

Practical application #4

A film consisting of manganese, cobalt and nickel in the mol ratio of 2 : 3 : 1 was formed over the surface of a SiO2 coated ** siliconware through the evaporation method as well as the electrodeposition method in the thickness of 100 micra. A rectangular pattern, 2 mm in width and 3 mm in length, was formed on the surface of the electrodeposition film through ( ) ** method, and the unnecessary parts were removed. After

that, the surface was oxidized in the atmosphere at 850 degrees C temperature for two hours. After printing and baking silver glaze paste at the both end of the rectangular piece, it was cut into 30 equal test pieces. The examination to check the thermistor characteristics of these 30 test pieces was conducted. The average resistance figure at 20 degrees C temperature was 53.4 K Ohm, and the fluctuation in the figure was within three percent. The average B constant was 5537, and the fluctuation in the B constant was within one percent.

Practical application #5

Barium and titanium were simultaneously but independently formed through evaporation through the electron beam method over the surface of a substrate made of a piece of pyrex glass. The condition of the evaporation was set so that the mol ratio of barium and titanium would be almost the same. Accordingly, a 7000 Å thick film was formed. The film was left in the atmosphere for three hours at 700 degrees C temperature in order to oxidize it. An X-ray examination revealed that the film was made of BaTiO3.

As clearly shown in the above examples of practical applications, the method to form a film of oxide according to this invention is quite easy. An extremely evenly formed film of oxide can be obtained according to this method. In

addition, thermistors which uses the films of oxide by this invention are far more advanced (improved) compared to the existing thermistors in interchangeability among thermistors which was considered difficult in the past. Furthermore, its application to dielectric materials enables small in size but large capacity capacitors.

4. Brief explanation of figures

No figures.

Application of correction

To: Director, Japanese Patent Office

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Patent Application #54-072039

2. Name of the invention:

A method to prepare a film of oxide

3. Person making the correction:

Relationship with the item: Assignee of the patent

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5. Date of the correction order:

August 4, 1979

6. Item to be corrected:

Line 19, Page 4 (of page 180)

7. Content of the correction:

"iron glaze paste" is changed to read "silver glaze paste"

[Translator's note]

Numerous letters and numbers have been found to be undecipherable due to the poor quality of printing of the original text. These letters and numbers are marked with **.

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15. Supplementary Notes

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16. Abstract

This invention pertains to a method for producing metal oxide films characterized by the fact that the metal elements constituting the main metal alloys contain at least one kind of transition element, and that the metal elements which constitute said metal alloy are thin films of barium and titanium in almost the same mol ratio.

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