United States Patent

Kohashi et al.

[15] **3,669,907**

[45] **June 13, 1972**

[54] **SEMICONDUCTIVE ELEMENTS**

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[30] **Foreign Application Priority Data**

Dec. 7, 1966 Japan....................................41/80696

[52] **U.S. Cl.**..................................**252/518,** 117/229, 106/48, 252/519, 252/520

[51] **Int. Cl.**..**H01b 1/06,** C03c 17/00

[58] **Field of Search**.........................252/518, 519, 520, 521; 117/229; 106/39, 48, 49, 46 A

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[57] **ABSTRACT**

Semiconductive elements having a specific resistivity of the semiconductor range (that is, 10^5 to 10^8 ohm-cm) which have an ohmic resistance even in an considerably high electric field and are highly durable in adverse physical and atmospheric conditions, which are manufactured by heating a mixture of powder of vitreous binding material and powder of semiconductive metal oxide dispersed in the former powder. Further, the dielectric strength and the uniformity of resistivity of said semiconductive elements can be improved by adding, to the mixture, powder of an oxide whose conductivity is much higher than that of said semiconductive metal oxide.

4 Claims, 8 Drawing Figures

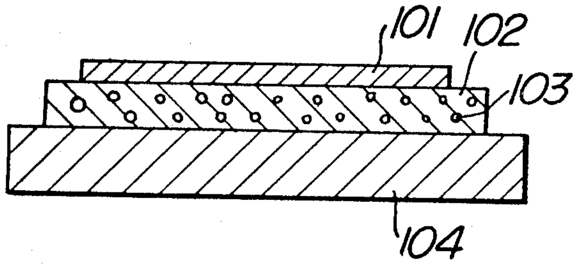


FIG. 1

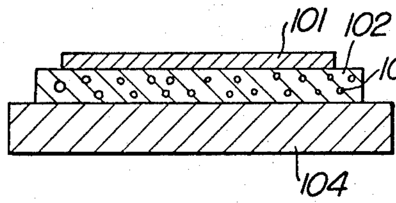


FIG. 3

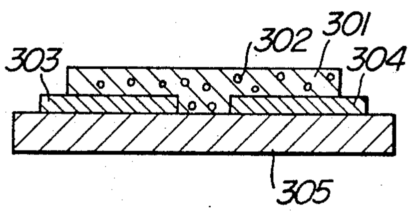


FIG. 2

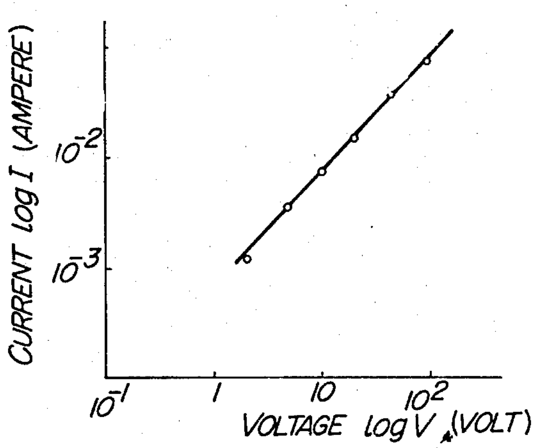


FIG. 4

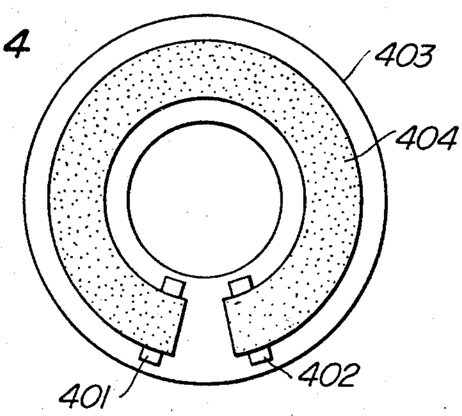


FIG. 6

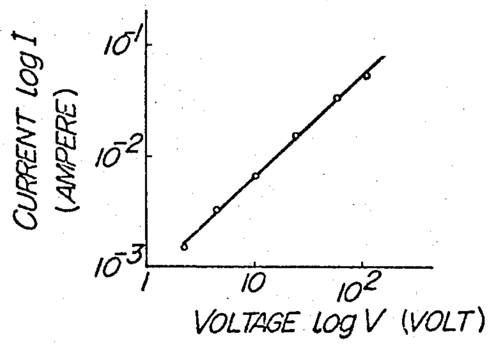


FIG. 5

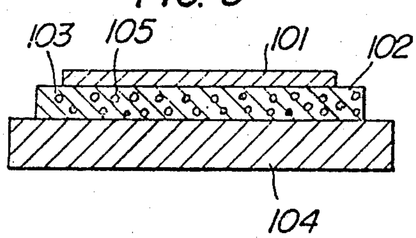


FIG. 7

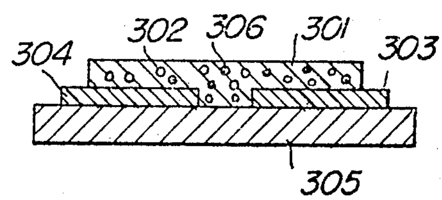
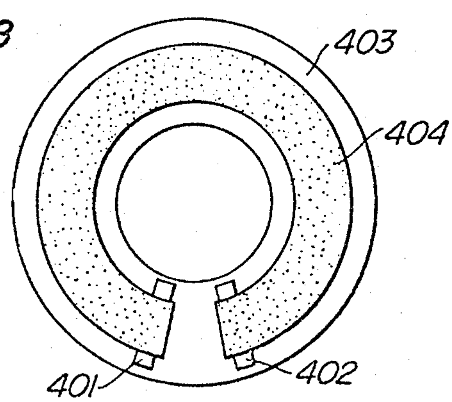


FIG. 8



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SEMICONDUCTIVE ELEMENTS

This invention relates to semiconductive elements, particularly to semiconductive elements which provide electric resistors with excellent properties.

One object of this invention is to provide semiconductive elements which are made from the mixture of a vitreous material and a semiconductive material or materials and which have an ohmic resistance of a specific resistivity of the order of 10^5 to 10^8 ohm-cm in the semiconductive region.

Another object of this invention is to provide a useful method for manufacturing the above-mentioned semiconductors.

The conventional conductive glasses which are made from the mixture of a vitreous material and powder of a metal, are intended to provide glasses which are very near, or as near as possible, to a conductor in resistivity, or semiconductive glasses with a directional resistivity whose specific resistivity is of the order of 10^5 to 10^8 ohm-cm and is in the range of a semiconductor but unaffected by an electric field. In the manufacture of the conventional semiconductive glasses, troublesome precaution must be taken about the processing atmosphere in order to prevent the powder of metal from being oxidized or degenerated because of the high temperature during the heating operation. Further, metals, generally having a high maleability, are very difficult to be pulverized beyond a certain limit with the present techniques of crushing or granulation. Moreover, with the conventional conductive glasses, control of the resistivity is very difficult because the resistivity of the metal is substantially low.

Another formation of the semiconductive elements is organic resins or plastics containing a conductive powder, the former serving as binder for the latter particles. Such a formation, however, presents an extremely non-linear voltage-current characteristics owing to the incomplete contact between the conductive particles and the binder, and to the surface state barrier of the conductive particles. Thus, the intended ohmic resistivity is not obtained by this kind of formation. Further, the temperature rise caused by an excessive current due to the non-linearity of the resistance, deteriorates the binding resin which is of low heat-resistivity, and shortens the life of the element.

According to this invention, new semiconductive elements which are highly resistive to the environmental conditions and have an ohmic resistivity in the semiconductive range (10^5 to 10^8 ohm-cm), are obtained by using a pulverized metal oxide as semiconductive material which is stable in an atmosphere of considerably high temperature and can be pulverized comparatively easily.

Now, this invention will be explained in detail with reference to the attached drawings, in which;

FIG. **1** is a sectional view of a semiconductive element embodying this invention;

FIG. **2** is a diagram showing the current vs voltage characteristics of the semiconductive element shown in FIG. **1**;

FIG. **3** is a sectional view of another embodiment of this invention;

FIG. **4** is a plan view of another embodiment of this invention;

FIG. **5** is a sectional view of still another embodiment of this invention;

FIG. **6** is a diagram showing the current vs voltage characteristics of the element shown in FIG. **5**;

FIG. **7** is a sectional view of another embodiment of this invention; and,

FIG. **8** is a plan view of another embodiment of this invention.

Referring to FIG. **1**, pulverized tin oxide (SnO_2) **103** is contained, as a semiconductive material, in vitreous binding material **102**. This semiconductive layer is formed by applying the mixture of the semiconductive material **103** and the powder of the vitreous material on the surface of iron plate **104**, and then dried by heating. The iron plate **104** of glazing quality serves as an electrode and at the same time as a heat-resistive substrate. Electrode **101** consisting of an electro-conductive paint is applied on the above-mentioned semiconductive layer.

Manufacturing steps for the above-mentioned embodiment of this invention will be described hereunder, by way of example. The composition of the mixture which consists of pulverized frit (hereafter referred to as A) as the binding material and pulverized tin oxide (hereafter referred to as B) as the semiconductive material, is shown in the following table.

Material	Percent volume
Pulverized frit:A	85%
Pulverized SnO_2:B	15%

The percentage of the metal oxide may be varied in the range of 10 to 35 percent depending on the desired resultant resistivity. The average grain size of A is preferably about 1 micron and that of B about 5 microns, at most. A larger grain size will cause less dispersion of the particles and a more difficult forming of the layer, resulting in a porous layer. On the other hand, a smaller grain size is desirable, presenting better dispersion, stable electric resistivity and easy forming. However, it should be noted that the conditions that the grain size of A is smaller than that of B should be maintained. If the grain size of A is larger than that of B, the particles of the frit will be covered with the particles of the metal oxide and will be prevented from contacting each other. Accordingly, the layer will not be formed when heated.

Next, the mixed powder of A and B thus measured is thoroughly stirred in a suitable mixing or stirring machine. In this example, the mixture of A and B added with a volatile liquid such as diacetone-alcohol or octyl-alcohol of equivalent weight was stirred in a ball-mill for 12 hours. A proper period for stirring is half a day to 1 day. A shorter period will cause insufficient dispersion of the particles, while a longer period will result in a less difference of grain size between A and B which is not enough to ensure the condition that the grain size of A is larger than that of B. Thus mixed and dispersed powder is substantially in a sol-like state, the liquid serving as dispersion medium. The mixture is applied on the surface of the heat-resistive substrate by the silk screen method which is a preferable method but to which this invention is not limited. The object of heating is to fuse the vitreous binder without solving the metal oxide particle into the vitreous material, and to cause the binding material to adhere to the substrate, forming a layer with a smooth surface. Thus, at least the surface portion of the metal oxide particles makes solid solution with the vitreous binder, thereby lowering the barrier in the surface of the metal oxide particles. This improves the electrical contact between the binding material and the semiconductive material, rendering an ohmic resistivity to the layer. A heating temperature as low as possible is preferable. Accordingly, a frit of lower viscosity in a low temperature, that is, of lower softening point should be selected. The following Table 1 shows the composition of the vitreous material used in this embodiment.

TABLE 1

Ingredients	%(weight)	Ingredients	%-(weight)
SiO_2	20.01	Na_2O	10.84
B_2O_3	28.58	K_2O	4.05
ZnO	18.33	TiO_2	2.31
BaO	14.34	Al_2O_3	0.41
CaO	0.74	Fe_2O_3	0.009
MgO	0.016	PbO	0.012

The softening point of this frit was about 600° to 640° C. An iron plate of approximately the same heat expansion coefficient as the vitreous binder was used as the substrate. Heating was performed in an electric oven without any difficulty. That is, the heating can be carried on in the atmospheric environment without necessity of any special arrangement, because tin oxide (SnC_2) used as the semiconductive material is very stable at a temperature around 640° C in the air and because the substrate used has substantially the same heat expansion coefficient as that of the vitreous material. The sol-like mixture of A and B is applied on the substrate and heated up to 650' C in about 20 minutes after being placed in an electric oven, during which the liquid component is evaporated leaving the mixture of powder on the substrate. The mixture on the substrate is maintained at that temperature (650° C) for about 5 minutes, followed by a cooling period of about 20 minutes, after which the whole process is completed. If a silk screen of 130 mesh is used for sieving the powder of about 1 micron in grain size, a layer of about 20 microns in thickness can be formed with one cycle of the heating. An additional layer can be made on the already formed layer, if required for some purposes. As the viscosity of a glass is considerably high, it will not occur that the first layer of the glass flows or changes in thickness at the temperature of 650° C during the short time of 5 minutes. FIG. 2 shows a current vs voltage characteristics of the semiconductive layer thus formed, the DC voltage being applied across the electrodes **101** and **104**. It will be seen from the excellent straightness of the characteristics that the layer has ohmic resistivity. This layer has a considerable large current bearing capacity, no doubt being heat-resistive.

FIG. 3 shows another embodiment of this invention in which titanium oxide (TiO_2) is used in place of the tin oxide of the previous embodiment. In FIG. 3, binder **301** is a vitreous material having a softening point of 550° to 580° C and contains pulverized TiO_2 dispersed therein. Transparent electrodes **303** and **304** are formed separately on the glass substrate **305** whose softening point is 680° to 700° C. A semiconductive layer consisting of binding material **301** and semiconductive particles **302** is formed over the electrodes and the substrate including the space between the two electrodes. The embodiment shown in FIG. **1** is intended to be a resistor across the thickness of the layer, whereas this embodiment shown in FIG. 3 is intended as a lateral pass for the electric current. Another feature of this embodiment is that the vitreous layer is formed on the surface of a glass or vitreous substrate. The method for forming the element and the requirements for the grain size are the same as in the previous embodiment.

As to the substrate, the material is limited to iron plate, ceramics and other similar materials in the previous embodiment, whereas glass is also usable in this embodiment. There are two conditions for a glass to be usable as substrate. One is that the softening point of the binder be lower than that of the substrate. This is an essential condition, because the forming will be impossible if the substrate softens earlier than the binder during the heating. The other condition is that the volume expansion coefficient of the substrate be approximately the same as that of the vitreous binder. If the expansion coefficients of both materials are significantly different, the substrate will crack from the strain caused during cooling, or at least the electrodes **303** and **304** will lose the conductivity owing to the strain. Table 2 shows the volume expansion coefficients and the softening points of the binder and the substrate used in this embodiment.

TABLE 2

	Expansion Coeff.	Softening point
Binding material	270×10^{-7}	appr. 580°C
Plate glass (substrate)	$(270–300) \times 10^{-7}$	650–700°C

In this example, the heating operation was performed at 630° C. The transparent electrodes (Nesa electrodes) **303** and **304** do not lose the conductivity through the heating.

FIG. 4 shows another embodiment of this invention, in which the element is formed in a shape suitable for a potentiometer. Transparent electrodes (Nesa electrodes) **401** and **402** are formed on the heat-resistive substrate (ceramics or glass) **403**. The semiconductive layer **404** which comprises a binding material containing pulverized metal oxide is formed on the substrate and the electrodes.

In these embodiments, the semiconductive material is not limited to tin oxide (SnO_2) or titanium oxide (TiO_2) as in the previous embodiments, but can be one of other semiconductive metal oxides such as WO_3, Sb_2O_5, Cr_2O_3, Fe_2O_3, V_2O_5 and Bi_2O_3, or a mixture of any two or more selected from these oxides.

It will be understood that this invention is not limited to the above-described embodiment, but can be embodied in variously modified formations according to the respective purposes.

As described above, this invention provides semiconductive elements wherein particles of semiconductive metal oxide are contained in a vitreous binding material. Owing to the fact that metal oxide is used for the component which imparts the conductivity to the element, the element has a high resistivity against severe environmental conditions, being stable even at a considerably high atmospheric temperature and accordingly can be manufactured without necessitating complicated and expensive equipment and operations. Thus, according to this invention, semiconductive elements are provided which have an ohmic resistance of a specific resistivity of the semiconductive range (that is, 10^5 to 10^8 ohm-cm), the resistivity being controlled by the relative volume of the metal oxide contained in the binding material.

In short, the semiconductive elements of this invention can be easily manufactured by a process comprising the following steps, that is; a step in which pulverized glass whose average grain size is smaller than 1 micron is mixed with pulverized semiconductive metal oxide whose average grain size is smaller than 5 microns but larger than that of said glass, the amount of the oxide being 10 to 35 percent in volume, and stirred with a volatile liquid additive until the mixture aquires a sol-like state; a step in which said mixture is applied in the form of a layer on the surface of a heat-resistive substrate whose melting point or softening point is higher than the softening point of said glass; and a step in which said layer of mixture is heated at a temperature higher than the softening point of said glass but lower than the melting point or softening point of said heat-resistive substrate. According to the method of this invention, the heating can be carried on in an atmospheric environment without necessity of any special consideration about the ambient conditions. Further, a smooth and strongly bound layer is obtained as the result of the fact that the grain size of the glass powder is selected to be smaller than that of the metal oxide powder. Moreover, the fact that the grain size of the glass powder and the metal oxide powder are smaller than 1 micron and 5 microns respectively, eliminates the possibility of producing a porous layer and ensures the satisfactory dispersion of the oxide particles into the binding glass, thus making possible the manufacture of resistors with uniform and reliable properties, and at the same time rendering the formation of the layer very easy. Thus, semiconductive elements having a specific resistivity of the semiconductor range (that is, 10^5 to 10^8 ohm-cm) can be produced in a very simple manner.

The semiconductive elements of this invention are stable even at a considerably high temperature and highly resistive against moisture and other ambient conditions.

In the following paragraphs, another aspect of this invention will be described with other embodiments.

In this aspect of this invention, a pulverized insulating material or materials are mixed with the above-described metal oxide powder in order to aid the dispersion of said metal oxide particles. According to this embodiment, extremely durable semi-conductive elements with uniform properties are obtained which have an ohmic resistance in the semiconductor range (10^5 to 10^8 ohm-cm) and have an improved dielectric strength. The insulating material to be mixed is only required to be thermally stable, since this material is used to prevent the incomplete dispersion or maldistribution of the oxide particles and in no way contributes to the conductivity of the element. Here again, the grain size of the glass powder should be selected to be smaller than those of the metal oxide powder and the powder of the insulating material. Mixing, application and heating of the powder are substantially the same as described in the previous paragraphs with other embodiments of this invention.

An example of this embodiment will be described hereunder with reference to the attached drawings. In FIG. 5, vitreous binding material **102** contains pulverized tin oxide (SnO_2) **103** as semiconductive material and pulverized $BaTiO_3$ **105** which is mixed in order to facilitate the dispersion or distribution of the semiconductive material **103** and to improve the dielectric strength of the element. The mixture consisting of powders of **102, 103**, and **105** is applied, in the form of a layer, on the surface of iron plate **103**, and then dried by heating. The iron plate **103** of glazing quality serves as an electrode and at the same time as a heat-resistive substrate. Electrode **101** consisting of an electro-conductive paint is applied on the above semiconductive layer. The composition of the mixture which consists of pulverized frit (hereafter referred to as A), the pulverized tin oxide (hereafter referred to as B) and the pulverized $BaTiO_3$ (hereafter referred to as C), is shown in the following table.

Material	Percent volume
Pulverized frit:A	65%
Pulverized SnO_2:B	15%
Pulverized $BaTiO_3$:C	20%

The percentage of SnO_2 may be varied in the range of 10 to 35 percent depending on the desired resultant resistivity, with a corresponding decrease in the percentage of frit. The same precaution as described in connection with the previous embodiments is required as to the grain size of B and C in relation to that of A. The procedures of mixing and stirring of the mixture, the ingredients of the frit and the heating operation in this example are substantially the same as in the previous embodiments. FIG. **6** shows a current vs voltage characteristics of the thus formed semiconductive layer, the DC voltage being applied across the electrodes **101** and **105**. The straightness of the characteristics shows that the layer has an ohmic resistance. This layer also has a considerably large current bearing capacity.

FIG. **7** shows another embodiment which is substantially the same as the embodiment shown in FIG. 3, except that pulverized Al_2O_3 is added in order to facilitate the dispersion of TiO_2 particles. Namely, binder **301** is a vitreous material having a softening point of 550° to 580° C and contains pulverized TiO_2 as the semiconductive material **302** and pulverized Al_2O_3 as the dispersing medium **303**. Electrodes of SnO_2 **304** and **303** are formed separately on the surface of glass substrate **305** whose softening point is 680° to 700° C. The semiconductive layer made from the powders **301, 302** and **306** also fills the space between the two electrodes. Other structural features of this embodiment are substantially the same as those of the embodiment described with reference to FIG. 3.

FIG. **8** shows another embodiment of this invention. This embodiment is substantially the same as the embodiment shown in FIG. **4**, except that the dispersing medium is added in the mixture. In FIG. **8**, transparent electrodes (Nesa electrodes) **401** and **402** are formed on the heat-resistive substrate (ceramics or glass) **403**. Then, the semiconductive layer **404** is formed on the substrate and the electrodes.

In these embodiments too, the semiconductive material is not limited to tin oxide (SnO_2) or titanium oxide (TiO_2) as mentioned above, but can be any one or any mixture of other semiconductive metal oxides such as WO_3, Sb_2O_5, Cr_2O_3, Fe_2O_3, V_2O_5 and Bi_2O_3. Also, the insulating or dispersing medium is not limited to $BaTiO_3$ or Al_2O_3, but can be any other material (for example, SiO_2) which has a much higher electric resistance than the above-mentioned metal oxide and a higher melting point than the vitreous binding material.

As described above, according to the second aspect of this invention are provided semiconductive elements wherein particles of a semiconductive metal oxide and particles of an oxide whose specific resistivity is higher than that of said metal oxide are contained in a vitreous binding material. Such elements have an improved dielectric strength and uniformity of resistivity owing to the sufficient dispersion of the semiconductive particles, besides the features described in connection with the previous embodiment according to the first aspect of this invention.

Such semiconductive elements can be easily manufactured by a process comprising the following steps, that is; a step in which pulverized glass whose average grain size is smaller than 1 micron is mixed with pulverized semiconductive metal oxide and pulverized oxide whose specific resistivity is higher than that of said metal oxide, the average grain size of said metal oxide and said oxide being smaller than 5 microns but larger than that of said glass, and the amount of said metal oxide being 10 to 35 percent in volume, and the mixture being stirred with a volatile liquid additive until said mixture acquires a sol-like state, a step in which said mixture is applied in the form of a layer on the surface of a heat-resistive substrate whose melting point or softening point is higher than the softening point of said glass; and a step in which said layer of mixture is heated at a temperature higher than the softening point of said glass but lower than the melting point or softening point of said heat-resistive substrate. Advantages obtained from such method have been described in connection with the first aspect of this invention, and therefore are not repeated here.

What we claim is:

1. A method for manufacturing a semiconductive element having particles of pulverized semiconductive metal oxide dispersed in a vitreous binding material comprising the steps of mixing a powder of glass with a powder of at least one semiconductive metal oxide selected from the group consisting of SnO_2, TiO_2, WO_3, Sb_2O_5, Cr_2O_3, Fe_2O_3, V_2O_5 and Bi_2O_3, whose grain size is larger than the grain size of said glass powder, the amount of said metal oxide being 10 to 35 percent in volume, until said particles of said metal oxide powder are well dispersed in said glass powder, and heating the mixture.

2. A method for manufacturing a semiconductive element having particles of pulverized semiconductive metal oxide dispersed in a vitreous binding material, comprising the steps of mixing pulverized glass, whose average grain size is smaller than 1 micron, with a powder of at least one semiconductive metal oxide selected from the group consisting of SnO_2, TiO_2, WO_3, Sb_2O_5, Cr_2O_3, Fe_2O_3, V_2O_5 and Bi_2O_3, whose average grain size is smaller than 5 microns but larger than the grain size of said glass, the amount of said metal oxide being 10 to 35 percent in volume; stirring the mixture with a volatile liquid additive until the mixture acquires a sol-like state; applying said mixture in the form of a layer on the surface of a heat-resistive substrate whose softening point is higher than the softening point of said glass; and heating said layer of mixture at a temperature higher than the softening point of said glass but lower than the softening point of said heat-resistive substrate, to thereby adhere said layer to said substrate.

3. A method for manufacturing a semiconductive element having particles of pulverized semiconductive metal oxide and of pulverized oxide whose specific resistivity is higher than that of a semiconductive metal oxide dispersed in a vitreous binding material comprising the steps of mixing powder of glass with powder of at least one semiconductive metal oxide selected from the group consisting of SnO_2, TiO_2, WO_3, Sb_2O_5, Cr_2O_3, Fe_2O_3, V_2O_5 and Bi_2O_3 and powder of an oxide whose specific resistivity is higher than that of said semiconductive metal oxide, the grain size of said metal oxide powder and said oxide powder being larger than that of said glass powder, and particles of said metal oxide and said oxide being well dispersed in said glass powder, and heating the mixture.

4. A method for manufacturing a semiconductive element having particles of pulverized semiconductive metal oxide and of pulverized oxide whose specific resistivity is higher than that of a semiconductive metal oxide dispersed in a vitreous binding material comprising the steps of mixing pulverized glass, whose average grain size is smaller than 1 micron, with powder of at least one semiconductive metal oxide selected from the group consisting of SnO_2, TiO_2, WO_3, Sb_2O_5, Cr_2O_3, Fe_2O_3, V_2O_5 and Bi_2O_3 and pulverized oxide, whose specific resistivity is higher than that of said metal oxide, the average grain size of said metal oxide and said oxide being smaller than 5 microns but larger than that of said glass, and the amount of said metal oxide being 10 to 35 percent in volume; stirring the mixture with a volatile liquid additive until said mixture acquires a sol-like state; applying said mixture in the form of a layer on the surface of a heat-resistive substrate whose softening point is higher but lower than the softening point of said heat-resistive substrate to thereby adhere said layer to said substrate.

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,669,907 Dated June 13, 1972

Inventor(s) Tadao KOHASHI et al

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

In the Claim for Priority, the following Japanese application should be included:

Japan, Patent Application No. 80697/66 filed on December 7, 1966.

Signed and sealed this 23rd day of January 1973.

(SEAL)
Attest:

EDWARD M.FLETCHER,JR.
Attesting Officer

ROBERT GOTTSCHALK
Commissioner of Patents

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