

April 7, 1970

HIROYUKI MATSUZAKI ET AL

3,505,632

INDIRECTLY HEATED THERMISTOR

Filed Dec. 6, 1967

3 Sheets-Sheet 1

FIG. 6

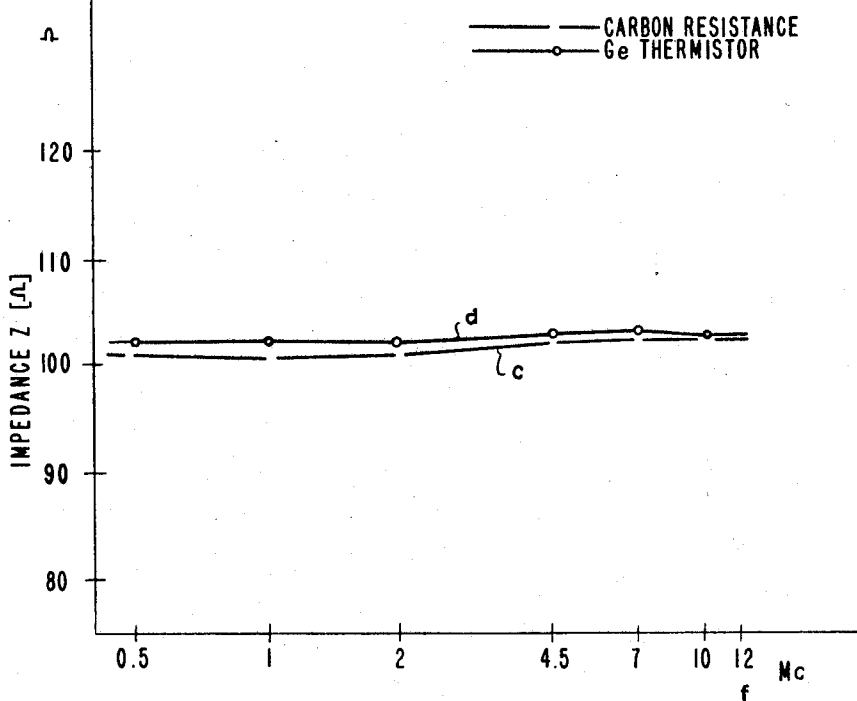


FIG. 1

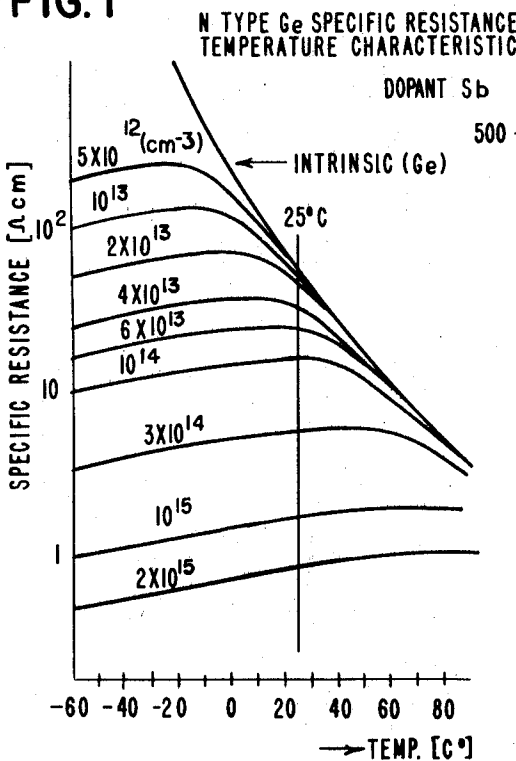
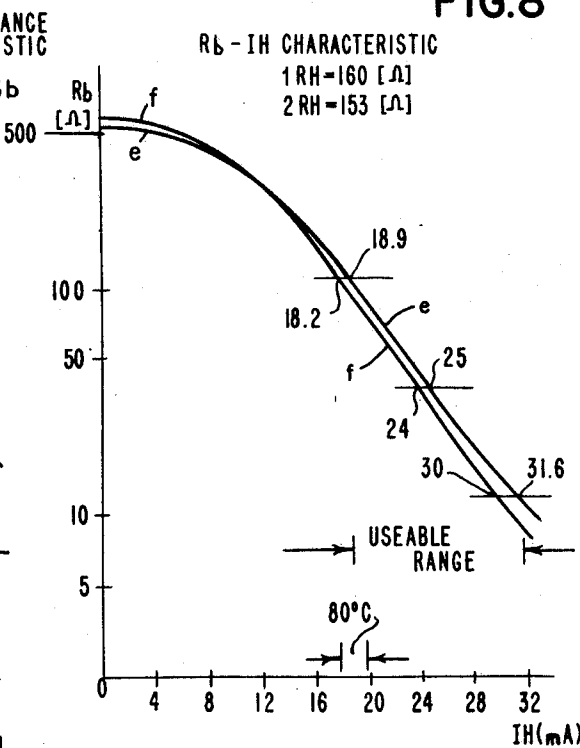


FIG. 8



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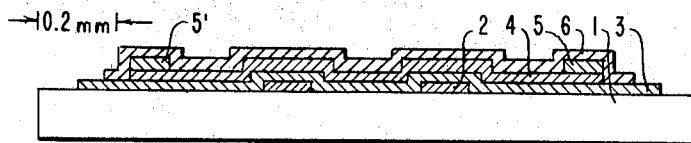


FIG. 2

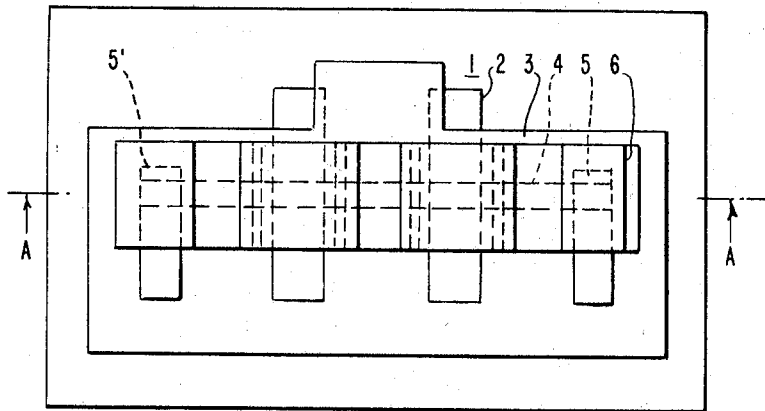


FIG. 3

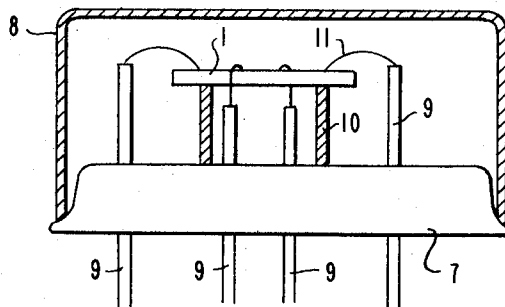


FIG. 4

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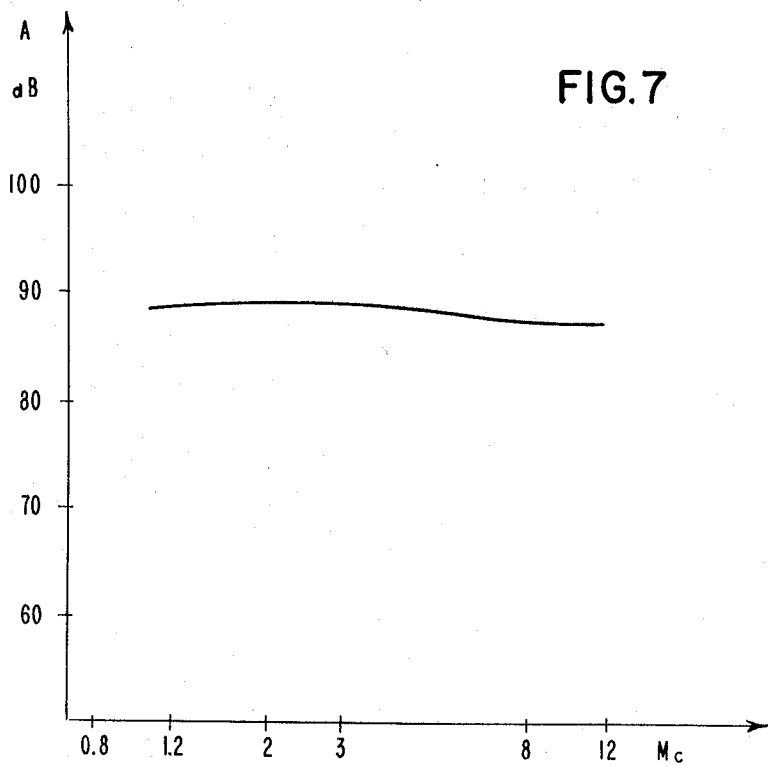
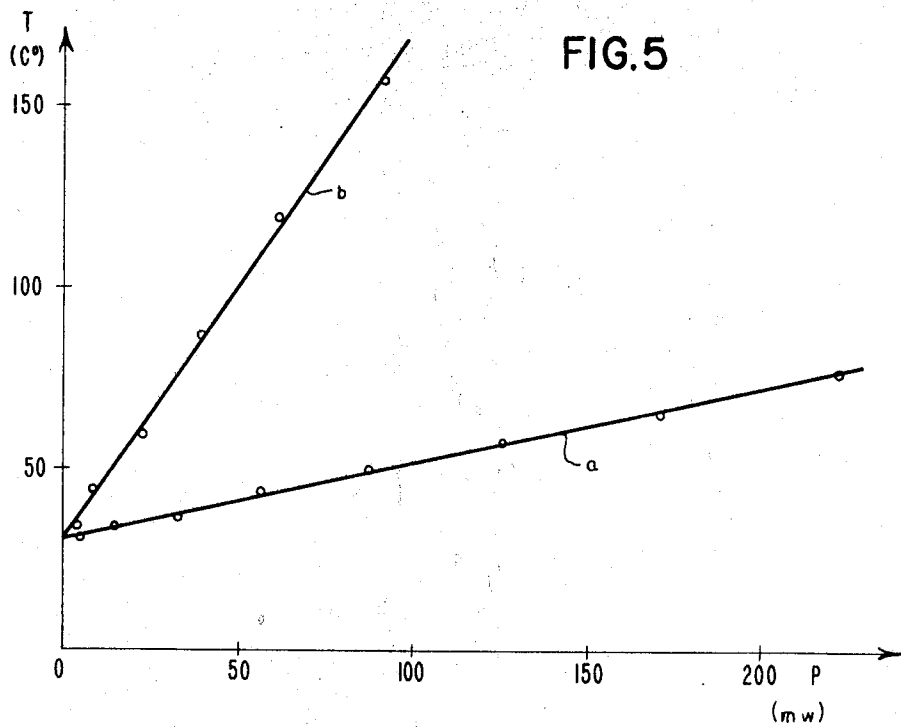
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## INDIRECTLY HEATED THERMISTOR

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41/80,893

Int. Cl. H01c 7/04

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2 Claims

### ABSTRACT OF THE DISCLOSURE

Described herein is an indirectly heated thermistor. The thermistor comprises a heating element, a thermistor element and an insulating film. This insulating film separates the heater from the thermistor element. The thermistor element is a semiconductor monocrystal, preferably a germanium monocrystal.

Our invention relates to an indirectly heated thermistor and, more particularly, to an indirectly heated thermistor in which the thermistor element is a semiconductor monocrystal.

Thermistors are electric elements for detecting temperature change and are used in many electric circuits. Conventional thermistors have all been manufactured by mixing oxides of metals such as manganese, nickel, cobalt, copper, iron, magnesium and titanium and firing or sintering them at high temperature.

However, thermistors of this type have defects in both their manufacture and use. The characteristics of thermistor elements vary very widely as to the grain size and purity, by the mixing conditions of said oxides, density of powder at the time of formation, firing temperature and profile. A very high precision of process control is required to manufacture a great number of thermistors having characteristics that are different from each other. Thus, great difficulties arise in the manufacture of thermistors.

Also, in many applications a larger "thermal time constant" is required. The time constant is influenced by many factors such as the heat capacity of the main body which supports the thermistor element and is thermally connected thereto and its heat radiation coefficient. It is also closely related to the diameter of the electrode leads of the sintered thermistor element and the atmosphere surrounding the element. In order to make the time constant larger, therefore, electrode leads of small diameter are used. This obviously reduces the mechanical impact strength of the thermistor, particularly in bead-type thermistors in which the leads support the thermistor element.

Accordingly, one object of our invention is to provide an indirectly heated thermistor having improved high frequency characteristics and mechanical strength.

Another object of this invention is to provide an indirectly heated thermistor wherein the thermistor element is not a sintered body and which possesses a constant temperature characteristic even when the allowable value of the specific resistance is large.

A further object of this invention is to provide an indirectly heated thermistor which can be easily manufactured with high reliability.

These objects are achieved by constituting the thermistor element by a single crystal semiconductor, thus improving the high frequency characteristic and mechanical strength. In accordance with our invention, electrodes are formed opposite each other on a single crystal semicon-

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ductor substrate whereby an arbitrary area in said single crystal semiconductor substrate operates as a thermistor element. A thin resistance film for indirectly heating said thermistor element through an insulating film is formed. This insulating film is coated before the formation of the thin resistance film. It is the important concept of this invention that a thermistor is constituted by a single crystal semiconductor. Thus, the thermistor element can obtain a uniform thermal sensitive characteristic without causing deterioration of high frequency characteristic. The single crystal semiconductor substrate has an impurity of concentrations as to exhibit a temperature characteristic of specific resistance which almost coincides with the specific resistance temperature characteristic of an intrinsic single crystal semiconductor in the desired operating temperature range. Thus, we obtain a uniform temperature characteristic that cannot be obtained by other means.

The method of formation of the indirectly heated thermistor of this invention is forming electrodes opposed to each other on a selected single crystal semiconductor so that the desired thermistor resistance may be generated. An insulating film and a resistance thin film are formed by evaporation in such a manner that the thermistor element and the resistance thin film may be insulated from one another by the insulating film.

Since our thermistor element is a single or monocrystal semiconductor, difficulties in manufacture which occur when utilizing a sintered body of metallic oxide as the thermistor element can be eliminated. Control of the process is extremely facilitated, so that danger of variation of impedance in high frequency caused by grain boundaries can be eliminated. Furthermore, since a semiconductor substrate is used as the main constituting body, said substrate can be firmly mounted on a metal stem through an intermediate adhesive. Therefore, the thermistor of this invention is suited for quantity production.

Other objects will become more evident from the following description of an embodiment of this invention with reference to the accompanying drawings in which:

FIG. 1 shows the temperature characteristic to specific resistance of single crystal germanium with various anti-impurity concentrations;

FIG. 2 shows a longitudinal section along A—A of FIG. 3;

FIG. 3 shows a plan view of a thermistor according to our invention;

FIG. 4 shows a thermistor firmly affixed to an adiabatic glass and sealed within a metal case;

FIG. 5 shows the relationship between the electric heating power and the temperature of a thermistor according to this invention sealed within a metal case;

FIG. 6 shows the relationship of frequency to impedance of the thermistor element of said thermistor;

FIG. 7 shows the relationship of frequency to the tertiary distortion of said thermistor element; and

FIG. 8 shows the relationship between thermistor resistance and heating current in an embodiment of this invention.

The scope of the invention is not to be limited to the described preferred embodiment.

Our invention utilizes a single semiconductor crystal which has the desired purity. A semiconductor material, of an impurity concentration exhibiting a specific resistance temperature characteristic that can be made equivalent to the specific resistance temperature characteristic of an intrinsic semiconductor material in the temperature range used, is used as the thermistor element. The semiconductor material used in this invention can be obtained by use of any of conventional monocrystal manufacturing techniques such as crystal pulling method, zone melting method and gaseous phase growth method. The material

can also be obtained by converting polycrystalline semiconductor material into a single crystal.

Basically, a monocrystalline semiconductor, whose purity has been made relatively high, as described above, is used as the substrate. Electrodes are provided opposite to each other so that the desired thermistor resistance may be formed. A resistance film for indirectly heating said thermistor element part is formed on the substrate. The thermistor element part and the resistance film are separated and insulated from one another by an insulating film formed by evaporation or high-frequency sputtering of an insulator. This insulating film is formed before forming the resistance film. Here, as in most other cases, the insulating film and the resistance film are laminated one upon another on one surface of the semiconductor substrate. At this time, the thermal time constant of the thermistor will become small. As in the formation of the insulating film, the resistance film is formed by evaporation or sputtering of a metal, such as nickel-chromium, on the upper part of said thermistor element. The thickness of the film is controlled so that the desired resistance value may be obtained.

A monocrystalline semiconductor, the purity of which has been made high properly, is used as the thermistor element. Germanium is used in the illustrative example as the monocrystalline semiconductor.

FIG. 1 shows specific resistance  $v.$  temperature characteristics of a germanium monocrystal with antimony impurity and of an intrinsic germanium monocrystal. In this figure, the abscissa  $T$  indicates temperature [ $^{\circ}$  C.] and the ordinate  $R$ 's indicates specific resistance [ $\Omega \cdot \text{cm.}$ ]. The curves show characteristics of intrinsic germanium and germanium with impurity concentrations of  $5 \times 10^{12}$ ,  $10^{13}$ ,  $2 \times 10^{13}$ ,  $4 \times 10^{13}$ ,  $6 \times 10^{13}$ ,  $10^{14}$ ,  $3 \times 10^{14}$ ,  $10^{15}$  and  $2 \times 10^{15}$ . As is evident from this figure, the temperature characteristic of germanium with an antimony concentration of less than  $10^{14}$ , coincides with the temperature characteristic of intrinsic germanium at a temperature higher than the greatest lower value, for example  $80^{\circ}$  C., of the normal temperature range wherein thermistors are used. This is seen to be a range of  $15-60\Omega \text{ cm.}$  Therefore, a thermistor with a uniform thermistor constant, temperature coefficient and specific resistance can be obtained by the use of a germanium with an impurity concentration of under  $10^{14}$ . At this concentration, the thermistor constant is  $4300^{\circ}$  K. in a temperature of above  $80^{\circ}$  C. which is equivalent to the activation energy of intrinsic germanium.

The thermistor constant  $B$  can be expressed as

$$R_1 = R_2 \exp B \left( \frac{1}{T_1} - \frac{1}{T_2} \right)$$

where resistance values are  $R_1$  and  $R_2$  [ $\Omega$ ] at the absolute temperatures of  $T_1$  and  $T_2$  [ $^{\circ}$  K.]. When the single crystal semiconductor is silicon, even if a single crystal of the highest purity now available is used, the temperature coefficient is positive until about  $300^{\circ}$  C. and the resistance variation factor is [ $1\%/^{\circ}$  C.] at the best. However, were it possible to increase the purity of silicon, it would become possible to obtain a characteristic that is equivalent to the temperature characteristic of an intrinsic silicon in a desired temperature range. Thermistors with the same temperature characteristic as the intrinsic semiconductor can also be obtained by using other semiconductor materials in the similar manner with the impurity concentration for obtaining a constant thermistor constant varying over a wide range. Our invention is based on this fact.

If a semiconductor material of an impurity concentration which exhibits the same specific resistance temperature characteristic as the intrinsic semiconductor is used in a desired temperature range, a constant thermistor constant can be obtained. This is the case even if the concentration is at an arbitrary value under a certain impurity concentration. In other words, thermistors having uniform temperature characteristics can be obtained with

the deviations of the impurity concentration of the semiconductor substrates. As described above, we provide a thermistor element of a semiconductor monocrystal, the purity of which has been made high properly.

An indirectly heated thermistor wherein the thermistor element is a semiconductor monocrystal according to this invention can be assembled into and attached to a metal stem of the same type used for the mounting of transistors by adhesives such as low melting glass or resin. The body holding the single semiconductor monocrystal substrate or a semiconductor monocrystal is firmly affixed by said adhesives and can be thermally separated from the metal stem. One end of the external lead wires of the thermistor element is connected to the electrode terminal in contact with the thermistor element and one end of the external lead wires of the resistance film is connected to the electrode terminal of said resistance film, whereby the mechanical strength of the indirectly heated thermistor can be greatly increased.

The thermal time constant of the thermistor of this invention is determined by the heat capacity of the thermistor including holding stand, atmosphere, and the thickness and heat conduction speed of the insulator separating the thermistor element from the resistor. This thermal time constant can be varied over a wide range by selecting the above elements at suitable values. The thermistor element is not held by the electrode lead wires but is attached to the thermistor holding stand through the base body holding the thermistor element part comprising the semiconductor substrate or semiconductor monocrystal.

According to our invention, we obtain a constant thermistor constant at a concentration under certain impurity concentration which could not be accomplished by the conventional method. This is an important advantage of our invention.

FIGS. 2 to 4 show an embodiment of an indirectly heated thermistor using the principles of our invention. FIGS. 2 and 3 show a thermistor body comprising a germanium monocrystal as the substrate with a thermistor element electrode, an insulating film, a resistance film and a resistance electrode sequentially formed on said substrate by evaporation. FIG. 2 is a section view taken along the line A—A of FIG. 3 which is a plan view. In actual production, many thermistors are simultaneously formed on the germanium substrate which is separated into individual thermistors upon completion of the evaporation by a scribe such as a diamond wafer scribe. For the sake of simplicity, however, only a single thermistor body will be described.

A germanium substrate including antimony impurities of a proper concentration was prepared as follows. Namely, a germanium ingot having an antimony concentration of  $5 \times 10^{13}$  was made by crystal pulling and was cut into individual wafers. Next, the wafer surface was polished by a No. 600 silicon carbide polisher. The wafer was then ultrasonically washed for 10 minutes in trichlorethylene and was dried for 10 minutes at  $80^{\circ}$  C. This germanium body is designated by 1 in FIGS. 2 and 3. This body was scribed to length of 1 [mm.], width of 2 [mm.] and the thickness of 0.25 [mm.].

Various materials are evaporated onto one surface of this germanium body. Thermistor element electrode 2 was formed by evaporation of a gold-antimony alloy in which the ratio of gold to antimony is 99.5 to 0.5% by weight in the evaporation source. A metal mask was used to prescribe the shape of the electrodes and determine the standard operating resistance value of the thermistor. In the present embodiment, the space between the opposite electrodes was 0.4 mm. and the standard operating resistance value was  $36\Omega$ . The thermistor constant was  $4300^{\circ}$  K. constantly.

Next, the evaporating source was changed from the gold-antimony alloy to silicon monoxide and a crucible, in which silicon monoxide was placed, was heated up to the evaporation temperature to form the insulating film 3

in FIGS. 2 and 3. The bell-jar of the evaporating apparatus was kept at about  $3\text{--}5 \times 10^{-6}$  [torr] and the semiconductor substrate was kept at  $200^\circ\text{C}$ . to increase the adhesiveness of the insulation film. Insulating film 3 of silicon monoxide was formed to a thickness of 6 [ $\mu$ ] through another metal mask and insulates the germanium wafer including the thermistor element part from resistance film 4.

Next, a resistance film for heating the thermistor element part indirectly is formed. In the present embodiment, this consists of a nickel-chromium alloy. Thus, a nickel-chromium alloy was used as the evaporating source and the semiconductor substrate was kept at  $200^\circ\text{C}$ . The resistance film 4, 1.8 mm. long, 0.1 mm. wide and 80  $m\mu$  thick, was formed through another metal mask so that it may be located on the central thermistor element part between the opposite electrodes. The resistance film 4 may also be of other metal materials. If the thickness of the film attached by evaporation must be limited to be extremely small and the reproducibility of the film is questioned, a material of a larger specific resistance such as, for example, a semiconductor can be applied and the thickness of the film can be made relatively large.

Next, gold electrodes 5, 5' were attached by evaporation as shown in FIGS. 2 and 3, to form the electrode lead-outs of resistance 4. In the present embodiment, the thickness of the gold film was 1 [ $\mu$ ]. A 200–300 Å. thick chromium layer (not shown) was evaporated on, as the ground for the attachment of gold, in order to insure better adhesiveness of gold. The resistance value of the resistor for heating the thermistor element part indirectly thus obtained was 200 [ $\Omega$ ]. A silicon monoxide film 6 was evaporated upon the nickel-chromium film to insure stability of the nickel-chromium resistance film at a high temperature.

Individual thermistors scribed out of a large semiconductor substrate may also be hermetically sealed to protect them from contamination. For this reason, the indirectly heated thermistor of this invention is hermetically sealed by the same assembling method currently used in the manufacture of transistors. There are several methods of attaching the semiconductor substrate firmly to the stem whereby the thermal coupling between the substrate and the stem is loose. FIG. 4 shows the outline of a thermistor firmly affixed to the stem by the use of a low working glass to provide thermal separation of the thermistor. In FIG. 4, 1 designates a germanium wafer as before, 7 designates a stem, 8 designates a cap, 9 designates wire leads for connecting the electrodes with the exterior, and 10 designates an adiabatic glass. 11 designates thin metal wires connecting the electrodes of the indirectly heated thermistor constituting body with wire leads 9. By thermally separating the thermistor constituting body from the stem as described above, the power loss of the resistor can be greatly reduced. This is seen in FIG. 5, wherein abscissa P indicates the electric power consumed [mw.] of the resistor; ordinate T indicates temperature [ $^\circ\text{C}$ ]. Curve a shows the characteristic of a thermistor constituting body, i.e. germanium disc, the back surface of which is directly soldered to the base and curve b shows the characteristic of a thermistor constituting body firmly affixed by the adiabatic glass as shown in FIG. 4.

FIG. 6 shows the frequency characteristics in the standard operation range ( $120\text{--}130^\circ\text{C}$ .) of an indirectly heated thermistor as an embodiment of this invention. Abscissa  $f$  indicates the measured frequency [mc./s.] and ordinate  $z$  indicates impedance [ $\Omega$ ]. c shows the characteristic of an ordinary carbon film resistor and d shows the characteristic of the present embodiment. As is evident from this figure, the indirectly heated thermistor of our invention has such an excellent frequency characteristic as coincides with the resistance value of a carbon film resistor.

FIG. 7 shows the frequency characteristic of distortion factor of the thermistor of this embodiment. The ordinate indicates the distortion-attenuation A [db] as against the third higher harmonic current of the fundamental wave current which flows when a high-frequency voltage is impressed on the thermistor resistance and the abscissa indicates the measured frequency  $f$  [mc./s.]. As is evident from this diagram, the tertiary distortion of the thermistor of this embodiment is one by several ten thousandths over a wide frequency band and the thermistor has an excellent high-frequency characteristic.

The excellence of the indirectly heated thermistor of this invention as a thermistor is seen from FIG. 8, wherein the relation between the heating current flowing through the resistor and the thermistor resistance is shown. The abscissa  $I_H$  indicates heating current [ma.] and the ordinate [ $R_b$ ] indicates thermistor resistance [ $\Omega$ ]. Curves e and f show the characteristics of thermistors of thermistor resistance of 540 [ $\Omega$ ] and 580 [ $\Omega$ ] respectively at  $25^\circ\text{C}$ ., wherein the resistance values of the resistors for heating indirectly are 153 [ $\Omega$ ] and 160 [ $\Omega$ ] respectively. The heating current flowing when the expansion factor that can be expressed by the ratio between a minute change of current  $\Delta I$  and a change of resistance  $\Delta R$  becomes constant at 17 [ma.] as is seen from this diagram and this corresponds to the heating temperature of about  $80^\circ\text{C}$ .. The least upper bound of the range of the heating current wherein this thermistor can be used is 32 [ma.].

The instant application is related to that of T. Matsumoto et al., Ser. No. 680,722 filed Nov. 5, 1967.

Only one of many possible embodiments of this invention has been described above. While the preferred embodiment has been described, it will be obvious to those skilled in the art that various changes and modifications may be made therein without departing from the invention described above, and it is aimed, therefore, to cover in the appended claims all such changes and modifications as fall within the true spirit and scope of the invention.

We claim:

1. An indirectly heated thermistor comprising a thermistor element, an electrical heater having electrical leads for indirectly heating said thermistor element, and an insulating film insulating and separating said thermistor element from said heater, said thermistor element being monocrystalline germanium of a specific resistance of  $15\text{--}60\ \Omega\cdot\text{cm}$ . at a temperature of  $25^\circ\text{C}$ . and having electrodes connected thereto, and said heater and said insulating film being thin evaporated films of metal and insulator respectively.

2. An indirectly heated thermistor comprising a monocrystalline germanium substrate having electrodes connected to said substrate, an insulating film formed on said substrate and a resistance film formed on said insulating film and connected to electrodes on said insulating film for heating.

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