

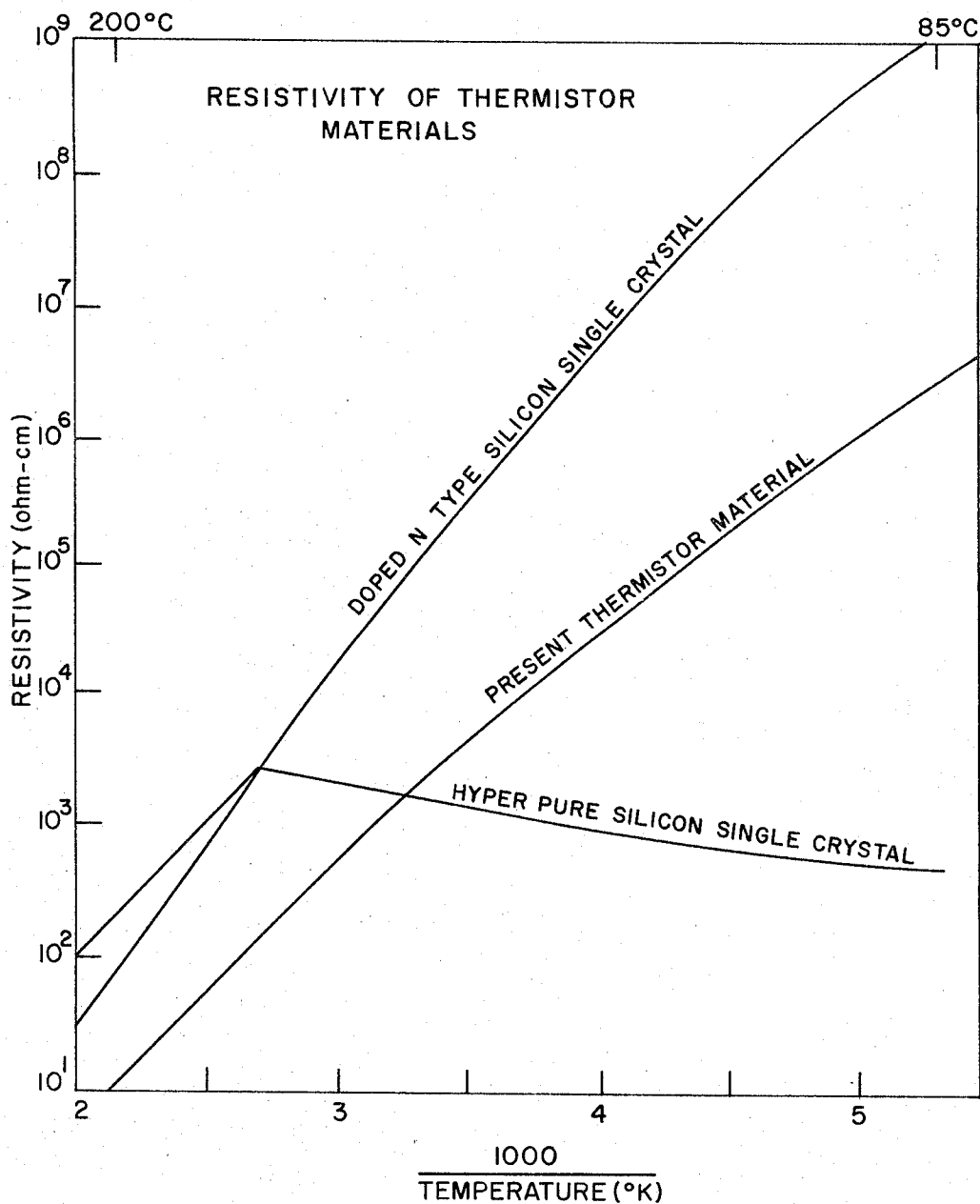
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SILICON THERMISTORS

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SILICON THERMISTORS

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3 Claims. (Cl. 338—22)

This application is a continuation-in-part of application Serial Number 131,816 filed August 16, 1961, now abandoned, and a division of application Serial Number 314,395, filed October 7, 1963, now abandoned.

This invention relates to thermistors prepared from N-type single crystal silicon and other semi-conductors which have a high negative temperature coefficient of electrical resistance and the process for preparing them.

Conventional semi-conductor materials are generally known as possessing negative temperature coefficients of resistance, that is, electrical resistance decreases as the temperature increases. These materials are characterized by only moderate changes in the resistance per degree centigrade. In other words, they require a substantial change in temperature before a marked change in total resistance occurs.

Conventional thermistors are now made from transition metal oxides by ceramic techniques. These metal oxides are semi-conductors. Their electrical resistance decreases as they are heated. The resistivity of a semi-conductor ordinarily follows the equation:

$$\rho = \rho_0 e^{\frac{E}{KT}} \quad (1)$$

where

ρ = resistivity in ohm cm. at temperature T in degrees Kelvin.

ρ_0 = constant in ohm cm.

E = activation energy or energy gap in the semi-conductor expressed in electron volts, and

K = Boltzmann's constant in electron volts per degree Kelvin.

Differentiation of this equation gives:

$$d\rho = -\frac{\rho E}{KT^2} dT \quad (2)$$

from which one gets:

$$\frac{1}{\rho} \frac{d\rho}{dT} = -\frac{E}{KT^2} \quad (3)$$

The left hand side of this equation represents the relative change in resistivity per unit change of temperature, which is the temperature coefficient of resistivity. This parameter is often designated by the letter alpha (α): mathematically it is given by

$$\alpha = -\frac{E}{KT^2} \quad (4)$$

Equation 4 indicates that the temperature coefficient of resistivity in semi-conductors is proportional to the energy gap and inversely proportional to the square of the absolute temperature. For any given temperature α is determined by the value of E. To express the values of α as a function of E, one can substitute K for its value in electron volts per degree Kelvin (8.61×10^{-5}) and T for the desired temperature in degrees Kelvin. For instance at 25° C. which corresponds to 298° K. one gets:

$$\alpha = -0.131E \quad (5)$$

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It is clearly seen that the value of α depends on the value of E, that is to say on the activation energy of the semi-conductor material used. To be practical as a thermistor material, the material should have a temperature coefficient (α) better than about $0.02 (\text{°K.})^{-1}$ at 25° C. In other words at 25° C. its resistivity should change with temperature at a rate of about 2% per degree Kelvin. This corresponds to an activation energy (E) of about 0.15 electron volt. Since the temperature coefficient varies inversely with the square of the absolute temperature (Equation 4), a thermistor material with a coefficient of 2% at 25° C. would only have a coefficient of 0.8% at 200° C. Present thermistors are made from semi-conductor materials with activation energies of less than about 0.3 electron volts. This means that at 25° C. the temperature coefficient of resistivity is less than about 4% per degree Kelvin. At higher temperatures such as for instance 200° C. the value of alpha drops to less than about 1.6% per degree Kelvin. The sensitivity of these thermistors is consequently limited. Besides the limited temperature sensitivity, present thermistors lack sufficient reliability, and particularly reproducibility. This is because present thermistors are made of polycrystalline aggregates of semi-conductor materials. These aggregates are formed by ceramic techniques. Such factors as crystallite size, shape, purity, degree of compaction and others affect the electrical properties of the material. Variations in these factors result in variations of the polycrystalline aggregates hence in variations of the properties of the thermistors made from them.

We have discovered a new type of semi-conductor material which does not have the limitations of present thermistor materials. This new type of semi-conductor material is made of N-type silicon. It makes possible a new and improved thermistor which is much more sensitive to temperature than conventional thermistors, and is reliable and reproducible.

The higher sensitivity is obtained because the activation energy (E) in our material is greater than 0.5 electron volt which gives a temperature coefficient of resistivity (α) greater than 6.5% per degree Kelvin at 25° C.

The superior reliability and reproducibility stem from the fact that our material is a single crystal of silicon prepared from hyper-pure silicon, an article of commerce (having 0.1 to 100 parts per billion of impurities) used in the fabrication of transistors, diodes, rectifiers, etc. The high crystal perfection found in these single crystals, together with the extreme purity of the starting silicon, increases the reliability and reproducibility of our material with respect to other thermistor materials which are polycrystalline and much less pure. Although we prefer our material to be in the form of single crystals, in which form it is superior due to the high degree of crystal perfection, and hence reproducibility and reliability, the fact is that because of its high activation energy (E) our material, even in polycrystalline form, is more sensitive than present thermistor materials. It is because of this superior sensitivity that polycrystalline N-type silicon when doped with gold, for example, is still a very useful thermistor material.

The starting single crystals of N-type silicon used in the preparation of our thermistor materials, is now available as large size single crystals. Such crystals may contain less than one part per billion of electrically active impurities which we call background impurities. By introducing certain metals such as gold, for example, as an impurity in single crystal silicon we have found that the resistivity is drastically affected. The background impurities no longer determine the electrical properties of the silicon. The added gold introduces new electronic energy levels in the silicon which completely change the

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electrical behaviour of the material giving rise to an activation energy (E) of about 0.54 electron volt. The resistivity of the gold doped silicon essentially follows Equation 1 in the temperature range of -100° to about 500° C. Equation 1 now takes the form:

$$\rho = \rho_{\infty} e^{\frac{0.54}{8.61 \times 10^{-5} T}}$$

or

$$\rho = \rho_{\infty} e^{\frac{6.3 \times 10^3}{T}}$$

The temperature coefficient of resistivity given by Equation 4 now becomes:

$$\alpha = -\frac{6.3 \times 10^3}{T^2}$$

which gives at 25° C.

$$\alpha = -7.1\% \text{ per } ^{\circ} \text{C.}$$

The thermistors prepared from gold doped N-type silicon have particular application in fields where high sensitivity is important. Our novel thermistor material exhibits this high sensitivity because of the location of the active gold level in the forbidden energy gap. This energy level gives an activation energy which is relatively large being approximately twice as large as that in the most sensitive commercially available thermistors.

The amount of impurity introduced as a dope in the silicon or other semi-conductor materials to effect the desired result mainly depends on the degree of purity of the starting material used. The impurity added should be in excess of background impurities so as to completely control the conductivity phenomena within the semi-conductor. When very high purity N-type silicon is used, the required gold level for example, may be as low as a few parts per billion. Useful thermistor materials can be prepared when the molar excess of doping element over background impurities is between 1 to 100 p.p.b.

There are several methods available for the introduction of impurities or doping in semi-conductor materials. Several techniques for quantitative doping are described in the literature. These techniques are normally operated at the melting point of silicon. A technique of particular interest is the zone leveling method which is very suitable for uniform doping with impurities of high partition coefficient such as gold. When variable doping levels are desired along the length of the crystal, one can use the crystal pulling technique or Czochralski method.

Both of these techniques are well described in chapters three and four of N. B. Hannay's work entitled "Semi-conductors" (Reinhold Publishing Corporation, 1959).

Our invention is further illustrated by the following specific but non-limiting examples.

Example I

A crystal of bar N-type silicon in the form of a rod of about $\frac{3}{8}$ inch in diameter and 9 inches long which had been previously refined by several passes in a floating zone scanner was used as a raw material in preparing a thermistor material. The resistivity of this single crystal bar ranged from about 40 ohms centimeter at the seed to about 60 ohms centimeter at the chuck end. This corresponds to an impurity level of about 1.5 to 1 parts per billion of equivalent excess phosphorus. The bar was oriented along the [111] axis. After a thorough etch to remove surface impurities from handling, the bar was placed in a conventional floating zone scanner. Between the seed and the bar, a total of 0.020 gram of pure gold was inserted. The gold was calculated to produce a molar concentration in the molten zone of 1.4×10^{-4} . One pass was then given by the scanner at the rate of 8 inches per hour under an argon atmosphere.

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The bar obtained was all single crystal oriented along the [111] axis and contained a uniform amount of gold equal to 4.2×10^{-9} moles of gold per mole of silicon or 4.2 parts per billion. This amount is calculated from the laws governing the segregation of impurities with very low distribution coefficients. The molar distribution coefficient of gold is 3×10^{-5} .

The doped silicon bar was nickel plated at the ends to produce good electrical contacts. The resistivity of the middle section of the bar was measured as a function of temperature using the two-point resistivity method.

In the two-point resistivity measurement, a current, I, is passed through ohmic contacts at the end of the sample and a voltage measurement, V, is made between two planes perpendicular to the current direction. Resistivity is then defined as the value ρ in the equation:

$$\rho = V/I \cdot A/L$$

where

ρ is the resistivity in ohm centimeters

I is the total current through the end contacts in amperes

V is the voltage between the two-probes in volts

L is the distance in centimeters between the two probes, and

A is the cross-sectional area (normal to the current I) in square centimeters.

The resistivity of the thermistor material prepared was measured in the range of -64° C. to 227° C. Table I gives the results obtained, together with the corresponding values of the temperature coefficient of resistivity.

TABLE I

Temperature ($^{\circ}$ C.)	Resistivity (ohm-cm.)	α (Percent per $^{\circ}$ K.)
-64	1.32×10^8	-14.1
0	8.25×10^7	-8.3
25	1.53×10^7	-7.0
60	1.44×10^6	-5.6
68	9.1×10^5	-5.3
84	3.9×10^5	-4.8
91	2.65×10^5	-4.7
95	2.36×10^5	-4.6
168	1.71×10^5	-3.2
169	1.66×10^5	-3.2
171	1.62×10^5	-3.1
214	4.41×10^4	-2.6
227	2.91×10^4	-2.5

A plot of the logarithm of the resistivity against the reciprocal of the absolute temperature gave a good straight line indicating that Equation 1 applied to this new material. The value of E, the activation energy, was calculated, using the least square method on the data from Table I. The value of E was found to be 0.53 electron volt which is consistent with the energy level introduced by gold in silicon (reported in the literature as 0.54 e.v.).

Using the value of 0.53 e.v. for E, one can calculate the values for the temperature coefficient of resistivity (α) at the various temperatures. These values are also given in Table I. It is apparent from these data that the resistivity of gold-doped N-type silicon greatly depends on temperature and that relatively small temperature variations produce rather large resistivity changes. It is obvious that gold-doped N-type silicon is a good thermistor material over the range of about -65° C. to about 250° C. since its resistivity varies by seven orders of magnitude in this temperature range.

Example II

This example is given for the purpose of comparing the material of our invention with hyper-pure single crystal silicon.

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A single crystalline bar of hyper-pure silicon was prepared by a vacuum floating zone technique. Sufficient number of passes were given to remove all impurities either by segregation or by evaporation, except boron which is not removed by this technique. The amount of boron in the silicon was calculated from mobility and resistivity measurements at 25° C. The boron level was about 0.2 part per billion which is in the range of the purest silicon commercially available.

The resistivity values obtained are given in Table II.

TABLE II

Temperature (° C.):	Resistivity (ohm cm.)
-66	670
25	1600
59	2240
66	2230
84	2400
92	2600
128	1350
152	534
175	346
195	279
202	170
227	120

It is apparent from an examination of these data that pure silicon exhibits a relatively small resistivity variation in the range of about -70° C. to about 140-150° C. In this range the resistivity increases with temperature, like metals do, instead of decreasing as intrinsic semiconductors do. At higher temperatures the resistivity begins to decrease as the pure silicon approaches the intrinsic range. At even higher temperatures the silicon becomes intrinsic and a sharp decrease in resistivity is observed. It is important to note that at best, hyper-pure silicon exhibits one order of magnitude change in resistivity in the range of about -80 to about 250° C., while silicon doped with gold exhibits a variation of the order of 10⁸. This very large variation underlines the importance of our discovery of the effect of doping silicon with gold.

Example III

The thermistor material made in accordance with the process described in Example I was compared to a conventional thermistor. Our gold-doped N-type silicon thermistor material had an energy gap of about 0.53 electron volt. The temperature coefficient of one such single crystal silicon which had been doped with gold is compared below with the calculated value for a conventional thermistor having an energy gap of 0.3 electron volt.

TABLE III
[Temperature coefficient]

Temperature (° C.)	Doped Silicon (Percent per ° K.)	Conventional Thermistor (Percent per ° K.)
-85	-17.5	-9.9
0	-8.3	-4.7
25	-7.0	-3.9
100	-4.5	-2.5
200	-2.8	-1.6

It is obvious from a comparison of these data that the thermistor material of our invention is vastly superior to conventional thermistor materials. This superiority is also shown graphically in the figure which compares the resistivity of the doped silicon single crystal of our invention with that of presently available thermistor materials and with that of a single crystal of hyper-pure silicon.

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Example IV

The method described in Example I was used to dope another N-type silicon single crystal. In this run the conditions were exactly the same as those set out in Example I except that 0.04 gram of pure gold was introduced into the molten zone. The silicon was doped using the same zone leveling technique as described in Example I. The silicon product gave the following resistivity versus temperature data:

Temperature (° C.):	Resistivity (ohm cm.)
0	8.2 × 10 ⁵
22	1.37 × 10 ⁵
25	1.07 × 10 ⁵
57	1.39 × 10 ⁴
104	1.45 × 10 ³
160	2.00 × 10 ²
180	1.00 × 10 ²

Again these data were plotted as log ρ vs. 1/T giving an excellent straight line. The least square method was used to calculate the activation energy (E). The value obtained was 0.53 electron volt which is in excellent agreement with Example I. It is obvious that, since the activation energy of this sample was the same as that of Example I, the corresponding temperature coefficient of resistivity would also be the same. It is apparent from an examination of these data that this was an excellent thermistor material.

Example V

Another run was made in which the single crystal silicon bar used was essentially identical to that of Example I except that it was doped with 0.1 gram of pure gold. The techniques used to prepare this thermistor were the same as the techniques described in Example I. The single crystal silicon bar prior to the doping had an N-type resistivity of about 40-60 ohms centimeter. The results of this run are shown in the table below:

Temperature (° C.):	Resistivity (ohm cm.)
0	2.36 × 10 ⁶
3	2.20 × 10 ⁶
25	3.12 × 10 ⁵
60	3.10 × 10 ⁴
91	5.70 × 10 ³
123	1.56 × 10 ³
150	4.90 × 10 ²
220	5.05 × 10 ¹

Example VI

Thermistors were prepared as follows: The gold doped silicon rod from Example V was cut using a diamond saw into small bars or parallelepipeds measuring 2.4 cm. x 0.4 cm. x 0.4 cm. These bars were nickel plated at the ends to insure good ohmic electrical contacts. Copper wire leads were soldered to the ends to complete the fabrication of the thermistors. The thermistors made were quickly screened by measuring their electrical resistance. All of them showed the expected response to temperature changes of gold doped silicon.

Obviously many modifications and variations of the invention, as herein above set forth, may be made without departing from the essence and scope thereof, and only such limitations should be applied, as indicated in the appended claims.

What is claimed is:

1. A thermistor of silicon having N-type polarity comprising copper leads soldered to a single crystal of N-type silicon metal plated at the ends and containing up to 100 parts per billion of background impurities and doped with gold.
2. A thermistor of silicon having N-type polarity comprising copper leads soldered to a single crystal of said

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N-type silicon nickel plated at the ends and containing less than 100 parts per billion of impurities doped with about 10 to 100 parts per billion of gold wherein the excess of gold over background impurities is between 1 and 100 parts per billion.

3. A process for preparing a thermistor having an activation energy of 0.54 electron volt which comprises selecting a single crystal of N-type silicon doping with about 10 parts per billion of substantially pure gold, using the zone leveling technique, cutting the doped crystal into a small bar, metal plating the ends of said bar to form good ohmic contacts, soldering a conducting wire to the metal coating at the ends of said bar to produce a thermistor device.

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