United States Patent

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[31] 117409

[54] **NEGATIVE-TEMPERATURE-COEFFICIENT RESISTORS IN THE FORM OF THIN LAYERS AND METHOD OF MANUFACTURING THE SAME**

5 Claims, 6 Drawing Figs.

[52] U.S. Cl. 338/25, 29/612, 29/620, 252/512, 338/22
[51] Int. Cl. H01c 7/04
[50] Field of Search 338/22, 23, 24, 25; 29/612, 620; 252/512

[56] **References Cited**

UNITED STATES PATENTS

2,860,219	11/1958	Taft, Jr. et al.	338/25 X
3,395,089	7/1968	Mayer et al.	29/620 X
3,435,399	3/1969	Gielisse et al.	338/22
3,472,074	10/1969	Glang et al.	338/25 X

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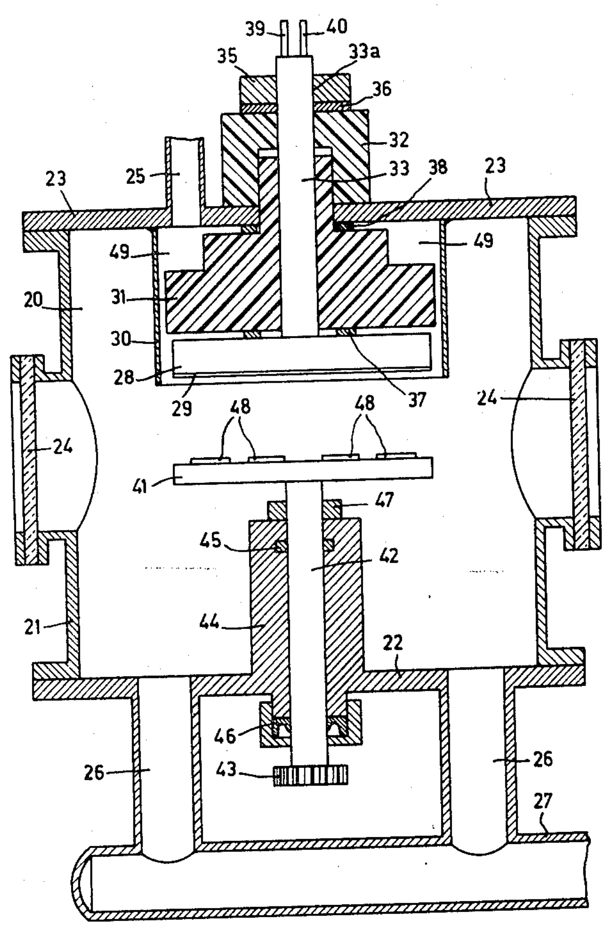
ABSTRACT: A negative-temperature-coefficient resistor formed by applying a thin semiconductive silicon carbide layer to a substrate.



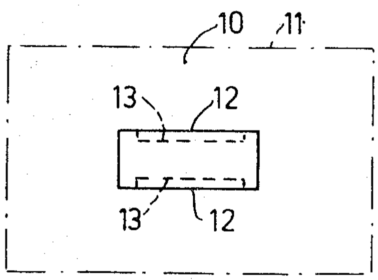


fig.1a

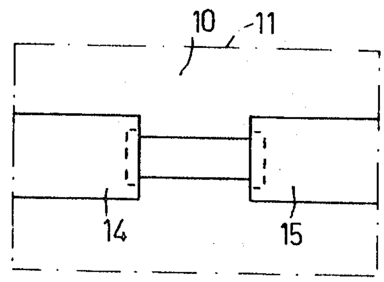


fig.1b

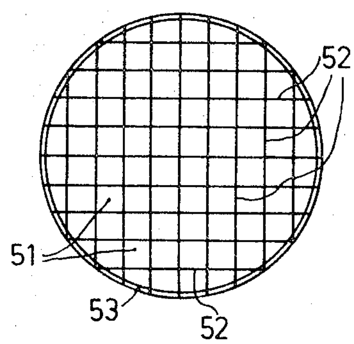


fig.3

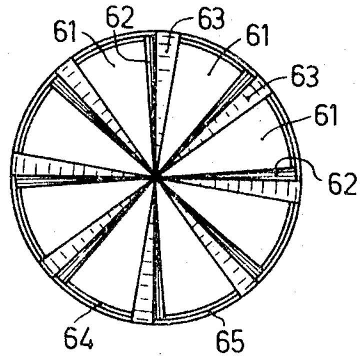


fig.4

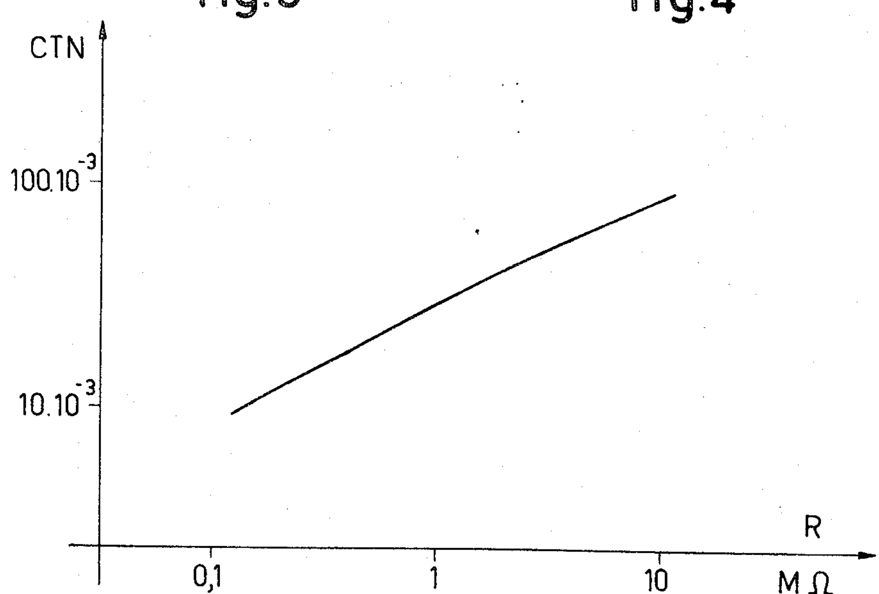


fig.5

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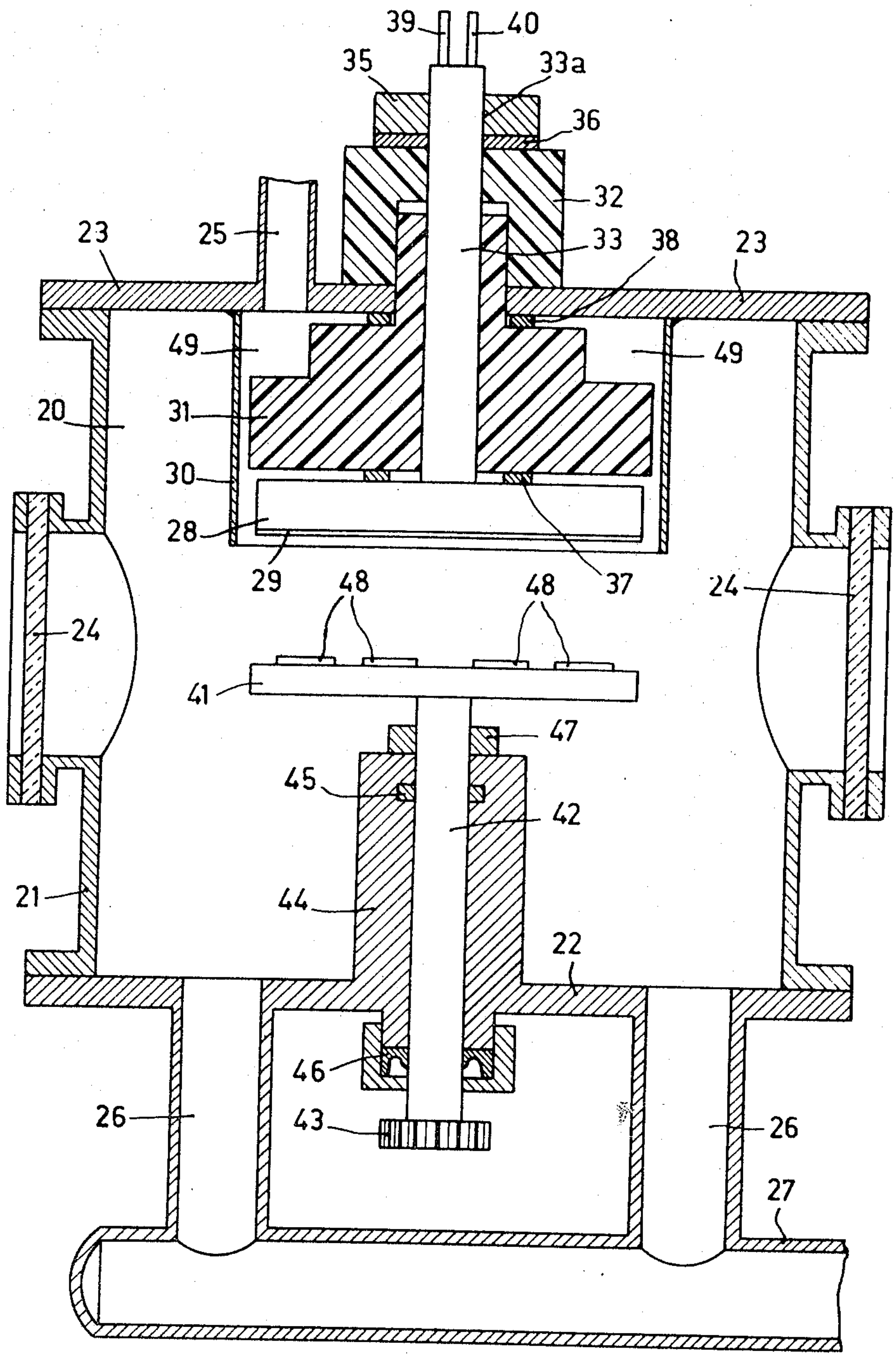

fig.2

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NEGATIVE-TEMPERATURE-COEFFICIENT RESISTORS IN THE FORM OF THIN LAYERS AND METHOD OF MANUFACTURING THE SAME

It is known that among the so-called passive electronic elements resistors having a negative-temperature coefficient of high value occupy a particular position between the active and passive elements. In connection with a change of the ambient temperature or rather with the variation of their own temperature in accordance with the ambient temperature and with the heat dissipation occurring in them, resistors having a high-temperature coefficient, when detecting a temperature variation, tend to stabilize currents or voltages or to vary them as a function of time in a definite sense.

Resistors having a negative-temperature coefficient, briefly termed NTC-resistors, have previously been manufactured by techniques known from the special ceramic manufacture. The desired negative-temperature coefficient has, in general, been obtained by using semiconductor oxides whose resistivity decreases with temperature. Among the many constituents used for obtaining NTC-resistors there may be mentioned by way of example:

a. solid solutions of Fe_3O_4 and materials having spinel structure such as Zr_2TiO_4 and $MgCr_2O_4$,
b. solid solutions of Fe_2O_3, Mn_2O_3 and NiO,
c. solid solutions of Fe_2O_3 and TiO_2,
d. solid solutions of NiO and/or CoO with small additions of Li_2O.

The raw materials are ground to a high degree of fineness and intimately mixed with the addition of a binder for facilitating the grinding process or for extruding the resultant paste.

After drying the moulded or extruded bodies are sintered at a high temperature in order to cause the oxides used to dissolve wholly or partly one in the other. The required electrical contacts are then provided by means of local coatings, for example, of a silver oxide paste, which is subsequently reduced by heating at an adequate temperature.

The resultant NTC-resistors are appropriate for mounting and uses corresponding with those of known resistors in the form of bodies or layers, but they are not suitable for being integrated in miniature circuits formed by thin layers in which the other passive elements such as resistors and capacitors are formed by thin layers deposited one after the other on a suitable substrate.

Moreover, the known NTC-resistors are not capable of following the temperature changes of the supporting body without great inertia, if they are employed for compensating the temperature fluctuations of the device in which they are used.

The present invention avoids the disadvantages of the known resistors and permits of depositing NTC-resistors in the form of thin layers on a substrate, which may furthermore be provided with deposits having a more or less high conductivity for the interconnection, with resistors without temperature coefficient and with the electrodes of fixed capacitors.

The NTC-resistors in the form of thin layers according to the invention are characterized in that they are formed by a thin silicon nitride layer having an impurity which eliminates the dielectric properties and renders the layer semiconductive. According to a further feature of the invention the silicon nitride layer is obtained by reactive cathode sputtering, while the doping element is formed by aluminum.

The NTC-resistors according to the invention may be applied to insulating substrates of various types such as glass, mica, ceramic material and, in general, on insulating material which does not exhibit troublesome development of gas in a vacuum of $10^{'7E'4}$ Torr. at a temperature of about 100° C.

Apart from the technique of applying the thin layer, the techniques known in the manufacture of microcircuits of thin layers may be utilized, that is to say, masking, etching, adjustment, if necessary, activating and surface protection.

The negative temperature coefficient of the applied layer depends upon the impurity concentration of the layer, which may be varied within very wide limits. Since a reduction of resistance of 1 percent per degree Centigrade is attainable, these resistors are very interesting, because it is possible to obtain a range of temperature coefficients from −1 percent to −8 percent per degree centigrade.

The resistivity of the applied layer, which is usually expressed in ohm per square, indicated by the symbol $R_{\square}$, depends both on the impurity concentration and the thickness of the layer. A resistance in ohm per square of a layer is, as is known, the constant resistance in the direction of length of a homogeneous layer when current passes through a square layer portion of any length from the side which is separated from the further part of the layer, a contact electrode being provided on each of two opposite sides of the square so that ohmic contacts of negligible natural resistance are obtained for this square.

Since the thickness of the applied layer can be varied within given limits, the resistivity and the negative temperature coefficient of the layer can be chosen freely to a given extent.

In view of the specific mechanisms involved in cathode sputtering only aluminum is employed as a dopant for the silicon nitride.

The resistivity obtained by high doping is attended with negative temperature coefficients of comparatively low values.

The values found for the temperature coefficients of layers of an average thickness as a function of the resistivity per square are indicated below.

$R_{\square}$	100 Ω	1 KΩ	10 KΩ	100 KΩ	1 MΩ	10 MΩ	100 MΩ
N.T.C. 10^{-3} per degree	0.3	1	3	10	25	50	100

The degree of doping is adjusted experimentally, which is possible by the fact that it determines mainly the resistance per square. The minimum and maximum thicknesses of the effectively employed layers vary in practice only in a ratio of not more than 1:5.

The conventional uses of NTC-resistors also apply to the resistors according to the invention and owing to their special structure they provide particular advantages such as the possibility of incorporation in a microcircuit of thin layers, of application to the envelope of an electronic part (transistor, thermally compensated quartz oscillator) which has to be stabilized thermally. Important is furthermore the possibility of following temperature fluctuations of the substrate without important thermal inertia.

The invention will now be described more fully with reference to the accompanying drawing.

FIGS. **1A** and **1B** are plan views of part of the surface of a substrate provided with an NTC-resistor according to the invention and the associated connecting elements.

FIG. **2** is partly an elevation and partly a sectional view of one embodiment of a device for the manufacture of the resistors according to the invention by reactive cathode sputtering.

FIGS. **3** and **4** are elevation of two different embodiments of the active surfaces of cathodes suitable for use in the device of FIG. 2.

FIG. **5** shows a curve indicating the relationship between the resistance per square of the layer and the temperature coefficient of the resistor with a constant layer thickness.

As is shown in FIG. **1A**, a surface element **10** of a larger substrate is bounded by a square **11**, indicated by broken lines. Inside the element **10** a silicon nitride layer with the dopant, for example, in a square form, is applied by means of suitable masking so that with this thickness the surface **12** of these dimensions and having the desired dopant has a resistance which is lower than the finally desired resistance. After the resistance of a sample square of the layer is measured, the reduction of the effective thickness of the layer is determined; this reduction can be carried out by etching with the aid of a photoresist or by microsandblasting of the edges of the layer in the direction of length of the square surface 12.

The effective width of the resistance strip after this calibration is indicated by the broken lines 13.

Subsequently, a very thin metal layer is applied from the vapor phase in vacuo, which layer satisfactorily adheres to the silicon nitride and the substrate. For this purpose, in general, a nickel-chromium alloy can be deposited with the aid of suitable masks. Then, for example, a gold layer may be deposited on the nickel-chromium layer in order to reduce the electrical resistance of the resultant connections. This gold layer may be deposited with the aid of the same masks as used for the deposition of the nickel-chromium layer. The connections obtained, which form at the same time the contacts with the doped silicon nitride, are indicated at 14 and 15 in FIG. 1B.

The device shown in FIG. 2 comprises an airtight space 20, in which an aluminum-doped silicon nitride layer can be deposited on a substrate by reactive cathode sputtering.

The airtight space 20 has a sidewall 21, supported from a socket 22, which is provided with means for connecting the space 20 with a high-vacuum pump (not shown). On the upper side the space 20 is closed by a metal plate 23 and the sidewall 21 is provided with windows closed by a transparent pane 24 of suitable thickness. The windows are arranged so that they can be opened and closed sufficiently rapidly. The electric discharges between the electrodes inside the space 20 in the diluted gas can be observed through the windows 24, while after opening, the windows can be used for introducing the substrates into the space and for removing them therefrom after the deposition of the silicon nitride layers. For the sake of simplicity the stuffing members between the various parts of the space 20 and the mounting parts are not shown.

The upper plate 23 is provided with a tube 25 for introducing the gas mixture into the space 20 to provide the diluted gas atmosphere for the reactive cathode sputtering. In these embodiments the means of communication between the space 20 and the high-vacuum pump (not shown) are formed by two tubes 26, opening out in a collecting space 27, which communicates with the high-vacuum pump via control valves (not shown) for the pumping rate.

The device shown by way of example comprises a cathode 28 provided with a composite active surface 29. The cathode 28 is surrounded by a protective ring 30, which is directly secured to the plate 23, so that it is connected to earth. The cathode 28 is fastened to the plate 23 by means of a pair of insulating members 31 and 32, for example, of ceramic material having a high-alumina content. The cathode 28 is provided with a fastening pin 33 of comparatively great length, the upper portion 33*a* of which is provided with screw thread for facilitating mounting by means of a nut or a tapped ring 35 and a washer 36; the assembly is closed in an airtight manner by two connections 37 and 38. The cathode 28 has an internal liquid circulation system for cooling purposes. The cooling liquid is supplied and drained through channels 39 and 40, arranged on the upper part of the fastening pin 33.

The lower part of the electrode system is formed by a rotatable anode 41 on a shaft 42, which is provided at the lower projecting end with a driving pinion 43. The shaft 42 is rotatable in a guide 44, which forms a bearing and an airtight through connection, the stuffing being obtained by two connections 45 and 46. The height of the anode 41 and the distance between the cathode 28 and the anode 41 can be adjusted by means of a thrust ring 47, arranged on the shaft 42. The elements on which the aluminum-doped silicon nitride layers are deposited are formed by substrates 48, which are partly covered by the masks determining the configuration of the layers. External mechanical means (not shown), which engage the pinion 43, serve for rotating the anode 41 at the beginning of the deposition of the silicon nitride on the substrates bearing on the anode.

In cathode-sputttering aluminum has previously been considered as one of the rare metals which does not provide particular cathode-sputtering effect in diode configuration under operational conditions corresponding with those of the present example by normal discharges, that is to say, a combination of pressure, electrode spacings and current densities such that the space between the electrodes where the discharge is performed is about half that between the cathode and the anode.

The experiments and investigations leading to the present invention has shown that this experimental assessment is correct only on a first approximation and that in fact aluminum can be volatilized easily and to a sufficient extent to dope a silicon nitride layer in an adjustable manner, which is obtained by reactive cathode sputtering, the doping percentage varying in accordance with the ratio between the aluminum surface and the silicon surface obtained by the discharge.

FIGS. 3 and 4 show two possible embodiments of the composite active surface 29 of the cathode 28 of FIG. 2. The embodiment of FIG. 3 provides a constant ratio between the aluminum surface and the silicon surface and the embodiment of FIG. 4 permits of varying this ratio.

In the embodiment of FIG. 3 the surface corresponding with the interior of each square, for example, 51 is formed by silicon and the vertical and horizontal lines 52, which form a uniform network, correspond with an aluminum network of square mesh supported from an aluminum ring 53, which surrounds the cathode 28. The protecting ring 30 prevents the ring 53 from being exposed to the discharge between the cathode and the anode. The ratio between the active aluminum surface and the active silicon surface depends upon the ratio between the diameter of the aluminum wires used and the pitch of the mesh of the network. This ratio may be adjusted by varying one of the factors or both factors.

The silicon surface may be formed by a poly- or monocrystalline silicon plate or by stacked separate plates; hexagonal plates obtained from a substantially circular bar facilitate stacking of the elementary plates.

In the embodiment of FIG. 4 the silicon surface of the cathode is formed by a given number of identical circle sectors 61, between which aluminum sectors 62 and 63 are arranged. The sectors 62 are not completely visible, since they are partly covered by the sectors 63. The angles at the centers of the sectors 62 and 63 are equal to each other. The sectors 62 are connected on the outer side with a ring 64, which surrounds the body of the cathode 28 and the sectors 63 are connected with a ring 65, which is capable of rotating with slight friction on the ring 64.

By angular displacement of the ring 65 relative to the ring 64 the aluminum surface required for the volatilization may be doubled and in the same manner the percentage of doping of the silicon nitride layer may be doubled. It is particularly advantageous to construct the composite active surface 29 of the cathode as is indicated in FIG. 4. The anode 41 is caused to rotate during the vapor deposition in order to obtain satisfactory uniformity of the properties of the layers deposited on the various substrates.

In the examination of the properties of the deposited layers ratios between the silicon surface and the aluminum surface of 1/10 and 1/1 have been tested.

The gas mixture introduced through the channel 25 into the space 20 consists preferably of argon with an addition of 7.5 percent by volume of nitrogen. This mixture is introduced into the circular space 49 so that the gas is homogeneously distributed around the cathode 28.

The device shown by way of example may be modified in various ways, for example by using a cathode having a smaller diameter than the anode, while the axis of the anode is displaced relatively to the cathode, the anode being independently rotatable for obtaining a uniform deposit on the whole surface.

A removable mask (not shown) permits of preparing the cathode for the volatilization by a predischarge in pure argon, while the anode is screened.

It is furthermore possible to control the resistance of the doped silicon nitride layer by providing the shaft 42 with an insulated ring located between the ring 47 and the body of the anode 41. A test plate is provided on the anode by connecting one of the contact members to earth and the other to the insulated ring by means of a wire passed through insulating beads. A tapping having an insulated output on the conductor 44 serves for measuring the resistance of the test surface so that the thickness of the layer in dependence upon the resistance can be accurately adjusted prior to the termination of the treatment and before the space again communicates with the ambience.

As stated above, the resistance per square of the deposited layer and the temperature coefficient with a given layer thickness depend upon each other so that the possibility of varying the layer thickness may contribute to restricting the results of this interdependence.

FIG. 5 shows on a logarithmic scale an example of a curve illustrating the relationship between the resistance per square of the deposited layer and the negative temperature coefficient thereof with a constant layer thickness. The values of the resistance per square are plotted on the abscissa and the values of the negative temperature coefficients in 1/1,000° C. are plotted on the ordinate.

The embodiments described above may, of course, be modified by using other equivalent technical means within the scope of the present invention.

What is claimed is:

1. A resistor having a negative-temperature coefficient in the form of a thin layer on a substrate characterized in that the resistor consists of silicon nitride, doped with an element which eliminates the dielectric properties of the silicon nitride and renders it semiconductive.

2. A resistor of claim 1, wherein the dopant is aluminum.

3. A method of forming a negative-temperature-coefficient resistor of claim 1 comprising depositing by cathode sputtering a thin layer of a doped silicon nitride on a substrate.

4. The method of claim 3 wherein the silicon nitride is doped with aluminum.

5. An electric element having at least one resistor consisting of a silicon nitride layer containing an impurity which renders said layer conductive.

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