July 6, 1971 YASUO SEKI ET AL **3,591,413**

RESISTOR STRUCTURE FOR THIN FILM VARIABLE RESISTOR

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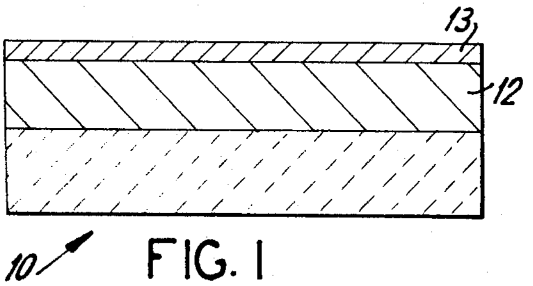

FIG. 1

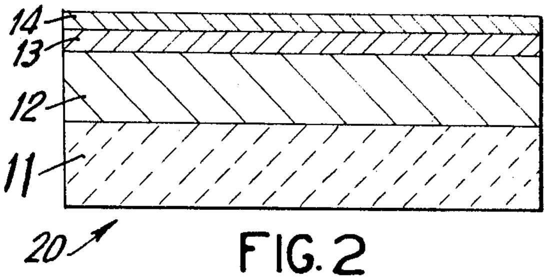

FIG. 2

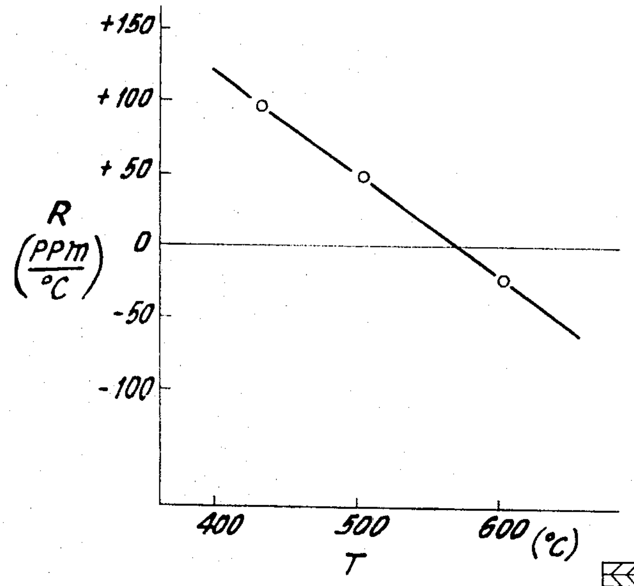

FIG. 3

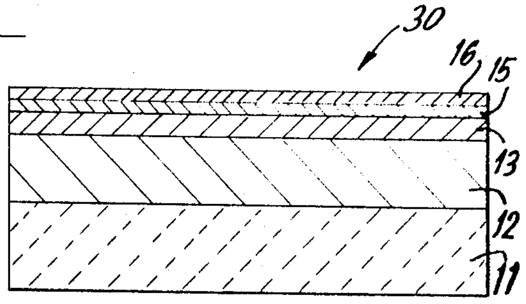

FIG. 4

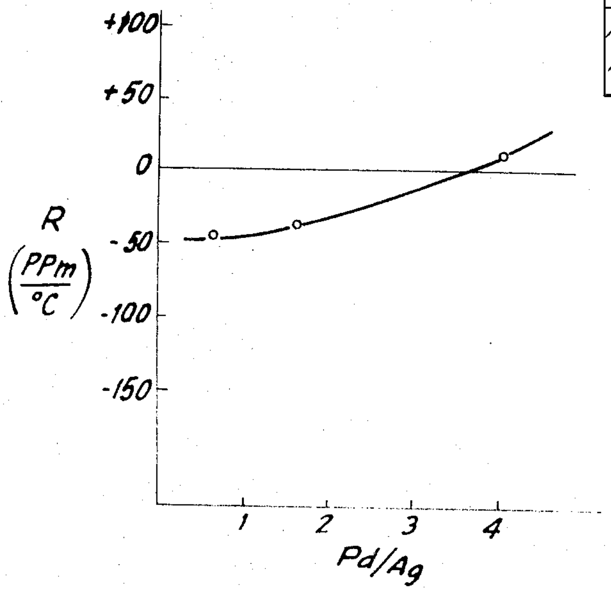

FIG. 5

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RESISTOR STRUCTURE FOR THIN FILM VARIABLE RESISTOR

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ABSTRACT OF THE DISCLOSURE

A thin film resistor structure for a variable resistor is described. The structure exhibits a low contact resistance and good temperature stability by employing a multi-layered construction. A tantalum nitride thin film layer is formed over an insulator substrate and is covered in turn with a thin film layer made of a low-resistive and anti-oxidation material. The composite multi-layered structure is then subjected to a heat treatment to diffuse or scatter the low-resistive and anti-oxidation material in a surface region of the tantalum nitride. The final heat treated structure exhibits a low noise level when employed with a brush for obtaining a variable resistor. The heat treatment is further employed to impart a particular temperature coefficient of resistance to the structure. Several embodiments and examples are shown.

This invention relates to a resistor structure suitable for a thin film variable resistor structure to which a slide brush may be slidably attached.

In recent years, requirements have steadily grown for smaller, more dependable, and lower cost parts for communication apparatus. To meet such requirements a number of circuit elements using films have heretofore been proposed. With regard to variable resistors, efforts have been made to miniaturize and improve the reliability of conventional variable resistors of the small wire wound type using an advance wire. For instance, Cu-Ni alloy, and film variable resistors placed on substrates made of various films (such as Nichrome thermet grades) have so far been developed. However, there are still a number of problems to be settled before these new resistors can be put in use. For example, these thin film variable resistors are usable only within a limited working temperature range of −65° C. to +80° C. They also invariably have a contact resistance of more than 0.2 percent of the total resistance of the resistor and exhibit a sliding noise of over 3 millivolts. They exhibit material changes in the resistance values during a life test under load, and their power rating is low.

It is known that the resistive material for thin films is made of tantalum nitride to partially improve the defects of conventional resistors, as described for instance in "The Bell System Technical Journal," January 1964, pp. 127–142 and "Bell Laboratories Record," October–November 1966, pp. 305–311. The thin film made of tantalum nitride can readily be prepared by an active cathode sputtering process using a tantalum plate as a cathode. It is possible to provide the thin film resistor having a specific resistance within range of 50∼5000 $\mu\Omega$-cm. and a temperature coefficient within the range of −300∼+300 p.p.m./° C. by suitably controlling the conditions of the sputtering process. According to the characteristics of tantalum nitride as mentioned above, a thin film of tantalum nitride provides an excellent resistor both with regard to its reliability and temperature stability. Yet the variable tantalum nitride cannot be put to practical use because its specific resistance is so high and its surface tends to produce an insulative material such as tantalum oxide. As a result the conventional tantalum nitride thin film variable resistor has a high contact resistance and a high sliding noise.

The principal object of this invention is therefore to provide a resistor structure suitable for a thin film variable resistor which has a low contact resistance and a low sliding noise and which operates stably over a wide temperature range.

According to this invention, a resistor structure for a thin film variable resistor is provided wherein a film of tantalum nitride is formed as a resistor base on one major surface of an insulative substrate, such as glass or ceramic plate. A first metal or alloy layer of low resistivity and which is highly adherent to tantalum nitride is formed on the film at the upper surface region of the tantalum nitride. A second metal or alloy layer which has a lower resistivity and a greater anti-oxidation property than the first layer is formed on the first layer. The final structure is subjected to a heat treatment permitting diffusion and reaction to occur among the layers.

Experimental results have shown that contact resistance and sliding noise can be decreased by providing a surface of low resistance on the resistor structure for direct contact with a slide brush even if the specific resistivity of the resistor material is high. For this reason, the resistor structure of this invention has a film of tantalum nitride and a metal-rich contact layer obtained after forming a metal layer and thus subjecting the film and metal to a heat treatment. The metal of the metal-rich layer needs to be of low resistivity and a low tendency to oxidize in comparison with tantalum nitride.

Variable resistors employing the resistor structure according to this invention have a working temperature range of −65° C. to +125° C., small contact resistance and small sliding noise. Moreover the resistor structure of this invention can be used for higher rated powers than conventional thin film tantalum nitride resistors.

To facilitate an understanding of the above-mentioned features, the present invention will be described in conjunction with the accompanying drawings, in which:

FIG. 1 is a longitudinal cross sectional view of the first embodiment of this invention; FIG. 2 is a similar view of the second embodiment of this invention; FIG. 3 is a graph showing the temperature coefficient vs. heat treatment temperature characteristic curve of the resistor of the second embodiment; FIG. 4 is a longitudinal cross sectional view of the third embodiment of this invention; and FIG. 5 is a graph illustrating the relationship between the compound ratio of the third embodiment and the temperature coefficient of resistance.

Referring to FIG. 1, the thin film resistor structure **10** of the first embodiment of this invention is manufactured by the following process:

A film **12** of tantalum nitride is formed on a substrate of insulative material **11** such as glass or ceramics through the sputtering process. Over the surface of the film **12** is further deposited by a vacuum evaporation a thinner film **13** of a metal or alloy which is highly adherent to tantalum nitride, for example osmium, rhenium, iridium, rhodium, molybdenum, cobalt, manganese, vanadium, nickel, chrome, or Nichrome alloy. Next, the structure as a whole is heat-treated for diffusion and reaction.

The resistor structure obtained through the above mentioned process produces a metal- or alloy-rich layer of low surface resistance wherein the metal is scattered at the surface of the tantalum nitride film after the heat treatment. A variable resistor employing a slide brush to the resistor structure of this invention has excellent characteristics such as small contact resistivity and low sliding noise. Furthermore, the surface of the resistor structure is chemically inactivated. These characteristics are shown by the following example.

EXAMPLE 1

As an insulator substrate, a ceramic disc having a thickness of one millimeter and a diameter of 10 millimeters is used. It is washed in the usual manner to cleanly remove oil, grease and other impurities from the surface. In order to form a tantalum nitride film on this substrate, a diode cathode sputtering apparatus using a tantalum plate as the cathode is employed.

The sputtering conditions for this purpose are shown in Table 1.

TABLE 1

Total pressure of vacuum system $(Ar+N_2)$—4×10^{-2} torr
Partial pressure of nitrogen gas—1.72×10^{-3} torr
Distance between anode and cathode—80 mm.
Inter-electrode voltage—3.5 kv.

Under the conditions above tabled and using an evaporation mask, a thin film of tantalum nitride of horseshoe shape with a film thickness of 3000 A., width of 1 mm., and length of 25 mm. is formed on the substrate. Over this film a thinner layer of nickel is deposited to a thickness of 150∼200 A. by vacuum evaporation using the same evaporation mask as employed for the film of tantalum nitride, thereby forming a two-layer film structure.

The resistor structure thus formed is heat treated in a vacuum at 400° C. for 3 hours and thereafter in air at 300° C. for 3 hours. Lead terminals for this structure are provided by terminals consisting of Nichrome alloy layer of a few hundred angstroms and a gold layer of a few thousand angstroms in thickness, both being successively coated over the resistor structure on both ends thereof. The lead terminals are formed by vacuum evaporation on both ends of the horseshoe-shaped resistor structure.

The resulting resistor element has a resistance of about 1.2 KΩ. The characteristics of the variable resistor are given in Table 2 and were determined by using a carbon piece having an area of 0.3 x 1 mm.^{2} as a slider brush and applying a pressure of 150 g. to the brush.

TABLE 2

Resistance value (Ω)	1170
Resis-temp coefficient (p.p.m./° C.)	−10
Contact resistance (percent)	0.15
Sliding noise (mv.)	2

The resistance of this structure can be controlled by varying the temperature for heat-treatments in vacuum and then in air. The temperature coefficient of resistance is controllable through a variation of the temperature in vacuo.

Referring to FIG. 2, a thin-film resistor structure **20** is obtained by further depositing to the structure of the first embodiment in FIG. 1 a low-resistive and anti-oxidizing layer **14** of metal or alloy of gold, platinum, palladium and silver, and thereafter subjecting the structure to heat-treatment. The resistor structure thus attained in his embodiment is highly reliable and high performance may be understood from the following example.

EXAMPLE 2

A horseshoe-shaped thin-film of tantalum nitride which has a thickness of 300 A., width of 1 mm. and length of 25 mm. is formed on an insulator substrate under the same conditions as with the first embodiment. On the film of tantalum nitride, thinner layers of Nichrome alloy and gold are successively deposited through vacuum evaporations to a thickness of 50 A. and 100 A., respectively. The resistor element thus formed consists of three layers, tantalum nitride-Nichrome-gold.

After that, the resistor structure is heat-treated in vacuum at 600° C. for one hour and thereafter in air at 300° C. for three hours. As lead terminals for this resistor element, terminal layers of gold are employed which may be

predeposited on both ends of the horseshoe resistor structure.

The resulting resistor structure has a resistance of about 1 KΩ. The characteristics of the variable resistor are listed in Table 3 and were measured with a carbon brush having contact area of 0.3 x 1 mm.^{2} and a contact pressure of 150 g.

TABLE 3

(Life test results obtained under application of ½W load at 85° C.)

Resistance value (Ω)	940.5
Temperature coefficient of resistance (p.p.m./° C.)	−31.0
Contact resistance (percent)	0.01
Sliding noise (mv.)	0.3
Life test (percent/2000H)	0.1

For comparison the characteristics of a resistor structure obtained without the heat-treatments in vacuum and in air are shown in Table 4.

TABLE 4

(Life test results obtained under application of ½W load at 70° C.)

Resistance value (Ω)	850
Temperature coefficient of resistance (p.p.m./° C.)	+100
Contact resistance (percent)	0.1
Sliding noise (mv.)	0.2
Life test (percent/1000H)	1

As will be understood from Tables 3 and 4, through the heat treatments the resistor structure is inactivated. This improvement may be explained on the basis of the condition of the surface of the resistor structure. In other words the low-resistive and anti-oxidation metals are scattered after the heating processes for diffusion and reaction. Thus, a metal-rich-layer is produced.

In this embodiment, if the structure is not heat-treated in vacuum, the temperature coefficient of resistance will have a positive value. Moreover, the temperature coefficient of resistance (R) of the structure may be varied by changing the temperature (T) during the heat-treatment in vacuum in accordance with the graph shown in FIG. 3. Therefore, the temperature coefficient of the resistance may be set to any arbitrary values by selecting the vacuum temperature of the heat treatment.

In addition, when it is desirable to control the temperature coefficient over a wider range, such control is easily attained by varying the sputtering conditions of Table 1. For instance a larger negative temperature coefficient can be obtained by increasing the partial pressure of the nitrogen gas. On the other hand, the temperature coefficient can be increased to a positive value by decreasing the nitrogen gas pressure.

Referring to FIG. 4, the thin film resistor structure **30** of the third embodiment of this invention is fabricated so that a silver layer **15** and a palladium layer **16** are successively evaporated in place of the gold layer **14** shown in FIG. 2. Then, a rich layer of silver and palladium is produced on the surface of tantalum-nitride layer through heat-treatment. According to this embodiment, the resistor structure is capable of varying its temperature coefficient with the compound ratio between silver and palladium.

EXAMPLE 3

Under the same dimensions and conditions as the Example 2, a resistor structure consisting of tantalum-nitride film **12** of 3000 A. thick and having a Nichrome layer **13** of 50 A. thick is prepared. In this example, the structure is further subjected to evaporation of a silver layer **15** of a thickness of 60 A., and a palladium layer **16** of a thickness of 200 A. Both ends of the structure are coated by Nichrome and gold for forming the terminal leads.

The resistor structure thus formed is heat treated in vacuum at 400° C. for 3 hours and thereafter in air at 300° C. for 3 hours.

The resulting thin film resistor structure has a resistance of about 1.2 KΩ, and the characteristics of the variable resistor are listed in Table 5 and were obtained by using a carbon brush having a contact area of 0.3 x 1 mm.^{2} and a contact pressure of 150 g.

TABLE 5

Resistance value (Ω)	1230
Temperature coefficient of resistance (p.p.m./° C.)	+20
Contact resistance (percent)	0.1
Sliding noise (mv.)	1

As mentioned above, the temperature coefficient of the resistor of this embodiment can be controlled by varying the vacuum heat treatment temperature similarly like that with the second embodiment. Furthermore, the coefficient is controllable through the variation of the ratio of silver and palladium as graphically shown in FIG. E.

The same temperature coefficient control is obtained by evaporating on the surface of the tantalum nitride film a previously prepared silver-palladium alloy followed by the heat-treatment in the manner of Example 2.

As has been described, the resistor structure for thin film variable resistors made according to the present invention has a low contact resistance, small sliding noise, excellent temperature coefficient, and high reliability, as compared with those of conventional thin film resistors.

We claim:

1. A resistor structure for a thin film variable resistor comprising an insulator substrate and a resistor film adhering to a surface of said substrate and consisting essentially of tantalum nitride, said film having at its outer surface a region into which a low-resistance and anti-oxidation material is scattered.

2. The resistor structure as recited in claim **1** wherein said material is selected from the group consisting of osmium, rhenium, iridium, rhodium, molybdenum, cobalt, manganese, vanadium, nickel, chromium and nickel-chromium alloy.

3. The resistor structure as recited in claim **2** wherein said region further includes a material selected from the group consisting of gold, palladium, silver, platinum and silver-palladium.

4. The resistor structure as recited in claim **1** wherein said material includes nickel-chromium alloy and a material selected from the group consisting of gold, palladium, silver, platinum and silver-palladium.

5. A resistor structure for a thin film variable resistor comprising an insulator substrate, a resistive thin film layer consisting essentially of tantalum nitride placed on said substrate, and a second thin film layer of low-resistive and anti-oxidation material placed over said resistive thin film layer, said second thin film layer being scattered throughout a surface region of said thin film resistive layer.

6. The device as recited in claim **5** wherein the second thin film layer of low-resistive and anti-oxidation material is selectively scattered throughout said surface region to control the temperature coefficient of resistance of said resistor structure.

7. The device as recited in claim **5** wherein said second thin film layer comprises

a pair of thin film metallic conductive layers overlying one another and the first thin film layer, with the layer adjacent the first thin film layer being substantially chosen for strong adherence to said first thin film layers and the uppermost of the pair of layers being selected to impart an anti-oxidation characteristic to the structure.

8. A method for forming a thin film resistive structure for a variable resistor comprising the steps of depositing on a substrate a thin film layer of resistive material consisting essentially of tantalum nitride, depositing on said resistive material a thin film layer of metallic low-resistive and anti-oxidation material, and applying heat for a predetermined duration of a range of 1–3 hours to said composite multi-layered structure and raising the temperature thereof to a preselected value of a range of 400° C.–600° C. to form a metal-rich contacting layer in a surface region of said resistive material.

9. The method as recited in **8** wherein said metallic low-resistive and anti-oxidation layer is formed with a thickness less than the thickness of said resistive thin film layer for diffusion and scattering of said metallic layer into said resistive layer.

10. The method as recited in claim **9** wherein said metallic low-resistive and anti-oxidation material depositing step further includes

depositing a first thin film metallic layer of conductive material over said resistive material, and

depositing a second thin film metallic layer of conductive material over said first thin film metallic layer.

11. The method as recited in claim **10**, wherein the heating step includes the steps of heating said composite multi-layered structure in vacuum for a preselected time of a range of 1–3 hours and at a selected temperature of a range of 400° C.–600° C. and heating said composite multi-layered structure in air for a selected time of approximately three hours and at a selected temperature of approximately 300° C.

12. A method for forming a thin film resistive structure for a variable resistor comprising depositing on an insulative substrate a thin film layer of tantalum nitride, depositing on said tantalum nitride layer a thin film layer of metallic conductive and oxidation-resistant material, applying heat for a predetermined duration of a range of 1–3 hours to said composite multi-layered structure and raising the temperature thereof to a preselected value of a range of 400° C.–600° C. to form a metal-rich layer in a surface region of said tantalum nitride layer.

13. The method as recited in claim **12** wherein the thin film layer over said tantalum nitride is deposited with a smaller thickness than said tantalum nitride layer.

14. The method as recited in claim **12**, wherein said heating step includes heating the composite multi-layered structure in a vacuum for said preselected time at said preselected temperature, and further includes heating the composite multi-layered structure in air for a preselected time of approximately three hours at a preselected temperature of approximately 300° C.

15. A method for forming a thin film resistive structure for a variable resistor comprising the steps of depositing on an insulative substrate a thin film layer of tantalum nitride, depositing on said tantalum nitride layer a first thin film layer of a material selected from the group consisting of osmium, rhenium, iridium, rhodium, molybdenum, cobalt, manganese, vanadium, nickel, chromium, and nickel-chromium alloy, and applying heat to said multi-layered structure for a predetermined duration of a range of 1–3 hours and at a selected temperature of a range of 400° C.–600° C. to form a metal-rich contacting layer in a surface region of said tantalum nitride.

16. The method as recited in claim **15** and further including the step of

depositing after the deposit of said first thin film material layer and before the heating step a second thin film layer over said first thin film layer,

said second thin film layer being made of a material selected from the group consisting of gold, palladium, silver, platinum and silver-palladium.

17. A method for forming a thin film resistive structure with a desired temperature coefficient of resistance variable resistor comprising the steps of depositing on a substrate a thin film layer of resistive material consisting essentially of tantalum nitride, depositing on said resistive material a plurality of metallic layers selected to provide oxidation resistance, adherence to said resistive material, and wherein a pair of metallic layers have thicknesses selected commensurate with a desired temperature coefficient of the composite multi-layered structure, and applying heat to said composite multi-layered structure for a predetermined duration of a range of 1–3 hours and to raise the temperature thereof to a preselected level of a range of 400° C.–600° C. to form a metal-rich contacting layer in a surface region of said resistive material and further control said temperature coefficient of resistance.

18. A method for forming a thin film resistive structure for a variable resistor comprising the steps of depositing on an insulator substrate a thin film of tantalum nitride, depositing over said tantalum nitride layer a thin film layer of Nichrome, depositing over said Nichrome thin film layers of silver and palladium in a predetermined ratio selected commensurate with a desired temperature coefficient of resistance, and applying heat for a predetermined duration of a range of 1–3 hours to said composite multi-layered structure and raising the temperature thereof to a preselected value of a range of 400° C.–600° C. to form a metal-rich contacting layer in a surface region of the tantalum nitride layer and to further determine the temperature coefficient of resistance of said structure.

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U.S. Cl. X.R.

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