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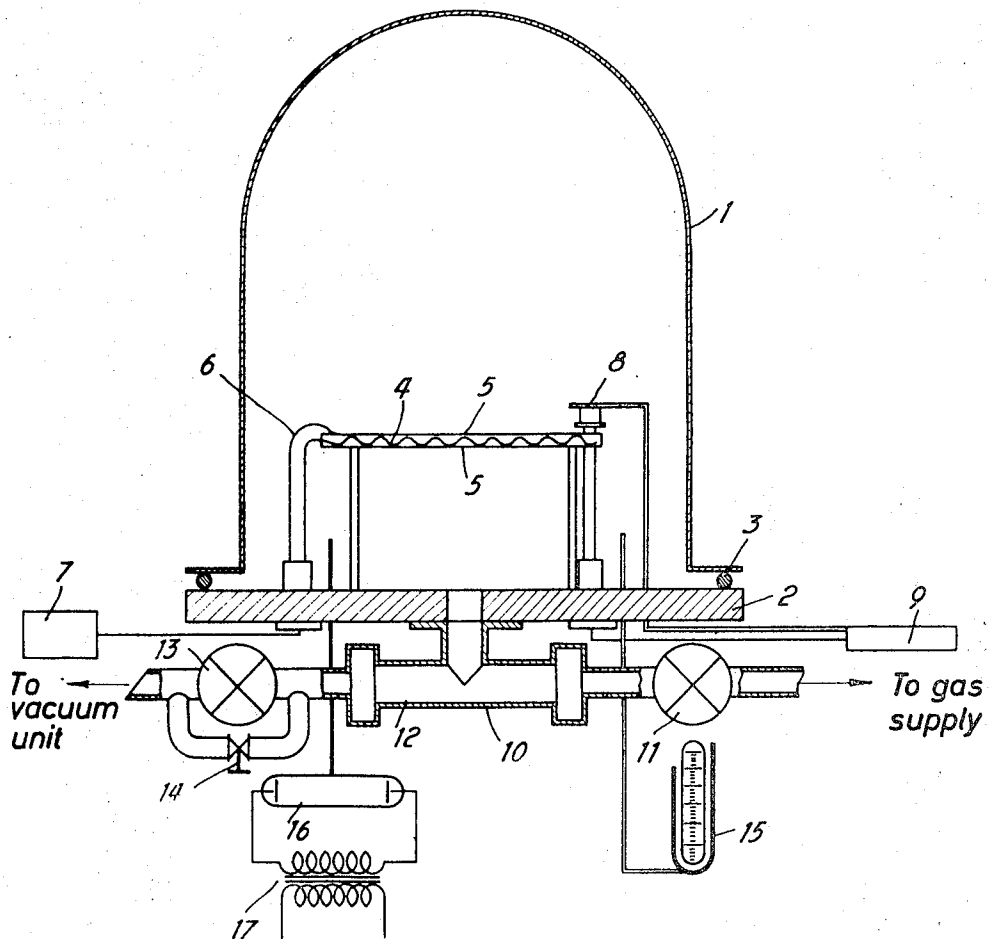
G. F. VULLIEZ ET AL
THIN LAYER RESISTORS

3,546,015

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2 Sheets-Sheet 1

Fig. 1



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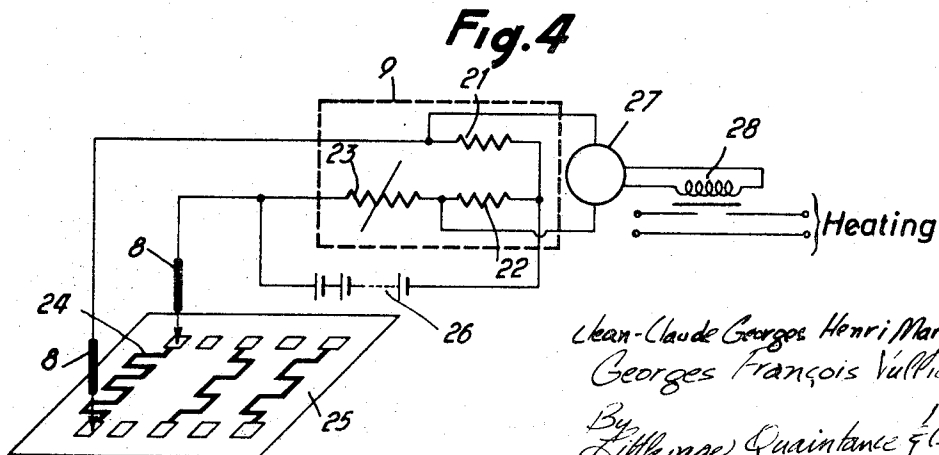
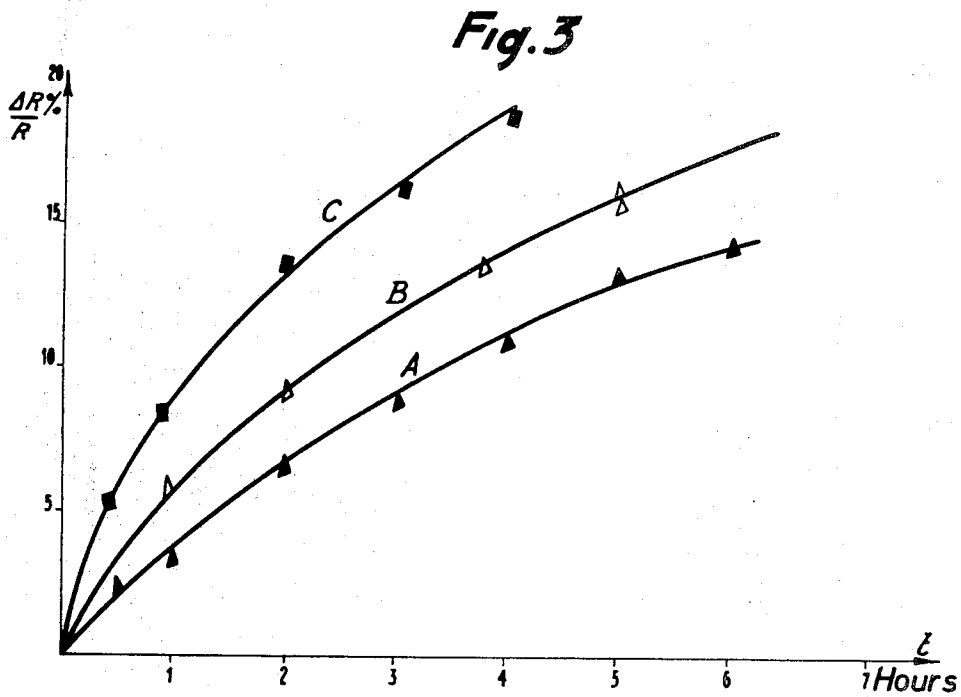
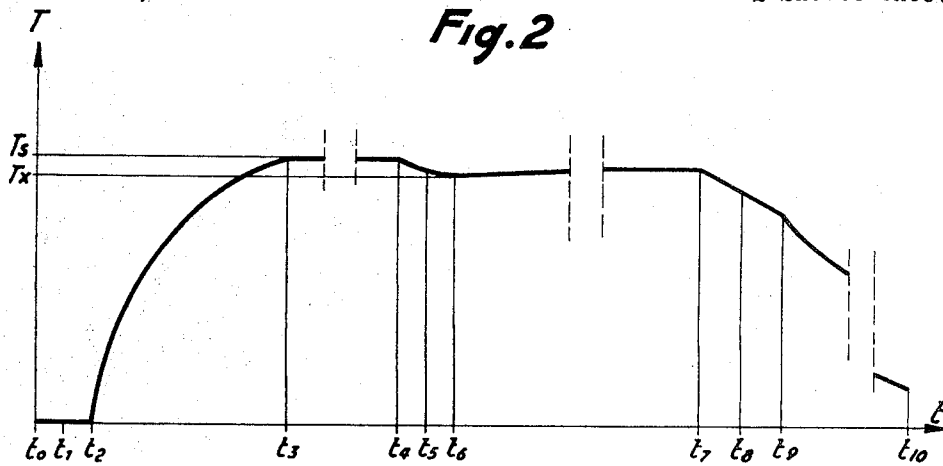
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THIN LAYER RESISTORS

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6 Claims

ABSTRACT OF THE DISCLOSURE

The resistance value of resistors formed of a thin metal layer is adjusted by means of a three step thermal oxidation process, each step succeeding the other in time without interruption, the first step consisting in heating the resistors at high temperature in a neutral atmosphere, the second step consisting in a controlled oxidation of said resistors in an atmosphere of oxygen gas and the third step consisting in cooling said resistors in a neutral atmosphere.

The present invention relates to a process for adjusting resistors during manufacture and, more particularly, to a process for adjusting thin layer resistors by thermal oxidation. The invention also relates to a device for carrying out said process.

In the known processes for adjusting resistors made of thin layers of metal or a metal compound, several successive steps are carried out on the thin layer deposited on a substrate, these steps consisting essentially in realizing a first oxidation in order to form a protective layer of oxide, thereafter subjecting said thin oxidized layer to stabilization heating in order to ensure the reliability of the resistance and, finally, carrying out further oxidation in order to adjust the resistance value of the resistors to their nominal value.

Both steps for oxidizing the thin layer of metal or metal compound are generally effected by means of an electrolytic process such as anode oxidation.

The stabilization heating adapted to ensure the reliability of the resistors is usually carried out in air for several hours and at temperatures which may be as high as several hundred degrees.

These known thin layer resistance adjusting processes have a certain number of drawbacks.

Firstly, the stabilizing temperature used is too low to abolish any deviation in the value of the resistance, especially when a resistor is adapted to be used at high temperatures, that is, higher than 150° C. A certain instability of the electrical characteristics results, and this disturbs the operation of the circuits in which these resistors are incorporated and, furthermore, compromises the efficient operation of the apparatus in which they are used.

The anodic oxidation steps carried out, on the one hand to obtain a protective layer and, on the other, to adjust the resistance value of the resistors only allow a relatively small number of resistors to be treated at a time, mainly owing to the size of thin layer resistors which are often very small.

Furthermore, the known processes are of necessity batch processes requiring a protracted time to carry them out as well as numerous and repeated manipulations resulting in high manufacturing costs.

This invention enables these drawbacks to be overcome, and relates to a process for reliably and accurately adjusting thin layer resistors made of metal or metal compounds by thermal oxidation.

The process of the invention consists essentially in heating the thin layer metal resistors in a neutral atmosphere, at a low pressure, maintained at a substantially constant value, referred to as the stabilization pressure, and at a temperature referred to as the stabilization temperature which is higher than twice the working temperature provided for; in maintaining the said thin layer so stabilized, after the said neutral atmosphere has been replaced by an oxygen atmosphere, at a temperature lower than the stabilization temperature, but remaining distinctly higher than the working temperature provided for, and in a pressure of oxygen approximately the same as the stabilization pressure, until the resistance of the said layer, which is continuously checked, has reached a predetermined value; and carrying out progressive cooling of the thin metal layer in a neutral atmosphere after the oxygen has been replaced by a neutral gas.

As a neutral gas it is advantageous to use argon, nitrogen or another gas which is neutral with respect to the thin metal layers used in the conditions of temperature and pressure of the process.

The process of the invention consists in a combination of three steps succeeding one another in time without interruption: a first high temperature stabilization step in a neutral atmosphere, a second controlled oxidation step in an oxygen atmosphere and a third cooling step in a neutral atmosphere.

Such a process has a certain number of advantages: one of these is that the use of stabilization temperatures more than twice as high as the working temperature provided for ensures an excellent stability of the electrical characteristics of the resistors, even in the case of the working temperature of said resistors being high, e.g. higher than 150° C. A second advantage arises from the fact that carrying out the steps of said process continuously results in a substantial gain in time and, consequently, lowers the unit cost price of said resistors.

Another advantage arises from the fact that exact and continuous checking of the value of the resistance during oxidation enables a rigorous adjustment of the nominal value of the resistances; this results in a considerable reduction in the percentage of manufacturing losses and, consequently, lowers the unit cost price of the resistors.

A device for carrying out the process of the invention can include, essentially, a sealed enclosure within which there are positioned means for heating said plates connected to temperature regulating means positioned exterior of the enclosure; means for continuously measuring the pressure in the enclosure; means for continuously measuring the value of the resistances, and connected to recording means positioned exterior of the enclosure; and means for alternately establishing a vacuum and a low pressure gaseous atmosphere within the enclosure.

The invention will be illustrated by the following description referring to the appended drawings wherein:

FIG. 1 is a diagrammatic cross-sectional view of a device for carrying out the process of the invention.

FIG. 2 is a diagram showing the successive steps used in the process of the invention.

FIG. 3 shows various relative relations of the value of the resistances during the oxidation step.

FIG. 4 shows a device for checking and adjusting resistance values during the various steps of the process.

As is seen in FIG. 1, a device for carrying out the process of the invention comprises a vacuum bell jar supported on a platen 2 by means of an O-ring 3. Within the vacuum bell jar is a heating element 4 positioned between two unoxidizable metal plates 5. Substrates on which the thin layer resistors are positioned, are arranged on the upper metal plate. A thermocouple 6 connected to a regulator device 7 positioned exterior of the vacuum

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bell jar 1 enables the temperature of both metal plates 5 to be checked and regulated.

A resistance measuring device 8 coacting with a measurement bridge 9 situated exterior of the vacuum bell jar 1 enables the oxidation rate to be adjusted and the thermal cycle to be stopped. An example of such a device will be described hereinafter with reference to FIG. 4.

The vacuum bell jar 1 can be connected, on the one hand, to a primary pump by means of a conduit 12, a valve 13 and a microvalve 14 in by-passing relation with 13 and, on the other hand, to the gas source by means of a conduit 10 and a valve 11. The pressure of gas in the vacuum bell jar is measured by means of a mercury manometer 15, and the vacuum is measured by means of a discharge tube 16 fed by a transformer 17; the assembly 15, 16, 17 may be replaced by a MacLeod gauge.

The device shown in FIG. 1 operates in the following manner for carrying out the process according to the invention: valve 11 being in a closed position and valve 13 in an open position, the atmospheric pressure in the vacuum bell jar 1 is lowered to a value of 10^{-2} to 10^{-3} torr. Valve 13 is then closed and the vacuum bell jar is filled with argon at a pressure varying from a few tens of torrs to a few hundred torrs by opening valve 11. Heating is then started by switching on the heating element 4. This heating is controlled by means of thermocouple 6 coacting with the control device 7.

Bell jar 1 is then evacuated and filled with oxygen at a pressure similar to that of the previous argon pressure. Heating is again applied at a lower temperature than the previous temperature and is discontinued when the resistance of the resistors reaches the predetermined value; the heating is then automatically cut-off by means of the resistance measuring device 8 coacting with the measuring bridge 9. The bell jar is again evacuated and is then refilled with argon, and the whole unit is allowed to cool to room temperature.

During these various steps the gas pressures are maintained substantially constant by means of the progressively adjustable microvalve 14. This microvalve provides a measured escape balanced by an arrival of gas. A needle-valve is suitable for use as a microvalve in accordance with the requirements of the invention.

FIG. 2, which is an operating diagram used in the process according to the invention, shows the variation of temperature T as a function of time t . The portion of the curve corresponding to the period of time t_0-t_1 represents the first primary pumping.

The portion of the curve corresponding to the period of time t_1-t_2 represents the filling with argon to the desired pressure, such as a few hundred torrs.

The portion of the curve corresponding to the period of time t_2-t_3 represents heating in an argon atmosphere.

The portion of the curve corresponding to the period of time t_3-t_4 represents the stabilization phase in an argon atmosphere. The curve has been broken by dotted lines to respect the scale of the diagram.

The portion of the curve corresponding to the period of time t_4-t_5 represents the second primary pumping.

The portion of the curve corresponding to the period of time t_5-t_6 represents the step of oxygen filling at a pressure of a few hundred torrs.

The portion of the curve corresponding to the period of time t_6-t_7 represents the adjustment phase by superficial oxidation.

The portion of the curve corresponding to the period of time t_7-t_8 represents the third primary pumping.

The portion of the curve corresponding to the period of time t_8-t_9 represents the second filling with argon at a pressure of several hundred torrs.

The portion of the curve corresponding to the period of time t_9-t_{10} represents cooling in an argon atmosphere.

The values of temperature T as a function of time depend on the characteristics of the thin layers used and the working conditions provided for. For instance, with

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a tantalum nitride thin layer 800 A. in thickness and effective to be used at temperatures of 150 C., or higher, the temperature levels suited to the requirements of the invention in the case of stabilization and oxidation pressures of 200 torrs are as follows:

Stabilization temperature T_s (heating with argon): 350° C., to 450° C., for a stabilization time of from about 1 to 10 hours,

Oxidation temperature T_x (oxidation): 250° C., to 380° C., for an oxidation period of from about 1 to 7 hours.

It should be noted that these thermal and pumping cycles can be made completely automatic.

Moreover, FIG. 3 shows the rate of relative variations of the resistance of thin layers of tantalum nitride of 800 A. thickness as a function of the duration of the oxidation phase, for various temperatures, and an oxidation pressure of 200 torrs. Curve A corresponds to a temperature of 320° C., curve B to a temperature of 350° C., and curve C to a temperature of 400° C.

The measurement of the thickness of the layer of oxide is carried out as follows:

The value of a resistance is measured in argon, before the oxidation step; let R be this value. The value of said resistance is measured in oxygen during oxidation step; let R' be this value.

Between the value of R and the value of R' measured during oxidation there are the following relations:

$$R = \rho \frac{L}{l \cdot e}$$

and

$$R' = \rho \frac{L}{l \cdot e'}$$

wherein:

ρ is the resistance of the material forming the thin layer; layer;

L is the length of the resistance;

l is the width of the resistance;

e is the thickness of the thin layer before oxidation;

e' is the thickness of the thin layer after oxidation.

The resistance has, therefore, increased by an amount R such that:

$$\Delta R = R' - R$$

The thickness of the thin layer has at the same time decreased by an amount Δe such that:

$$\Delta e = e - e'$$

These two variations are connected by the relation:

$$\frac{\Delta R}{R'} = \frac{\Delta e}{e}$$

If d_1 represents the specific weight of the material of the thin layer, d_2 the specific weight of the oxide formed and a the mass ratio of pure metal in the oxide, the thickness e of the said layer of oxide is given by the relation:

$$e = \frac{d_1}{d_2} \times \frac{1}{a} \cdot \Delta e$$

FIG. 4 shows the resistance measuring device 8 connected to the measuring bridge 9.

The measuring bridge 9, of the Wheatstone bridge type, comprises two fixed resistors 21 and 22, a variable resistor 23, the fourth arm of the bridge consisting of the thin layers resistance 24 positioned at the terminals of the adjustable point device 8. Resistance 24 selected as a reference is representative of all the resistances positioned on the substrate 25. The bridge is supplied with power by means of a D.C. generator 26, and the equilibrium of said bridge is regulated by a photosensitive galvanometer cell 27. This galvanometer being provided with a device 28 for automatically cutting off the heating.

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When resistance 24 has reached the predetermined valve, relay 28 automatically cuts off the heating.

It should be noted that the invention covers all other methods of carrying out such devices which are within the capacity of a man skilled in the art, seeing that these devices are designed for putting into effect the process described hereinabove.

We claim:

1. A process for adjusting thin layer resistors by thermal oxidation, comprising the steps of heating said thin metal layer resistor in a neutral atmosphere at a stabilization pressure lower than the normal pressure and maintained at a substantially constant level, and at a stabilization temperature at least twice as high as the working temperature for which the said resistance is intended, thus providing a stabilized thin layer; replacing said neutral atmosphere by an oxygen gas atmosphere; maintaining said stabilized thin layer at a temperature lower than said stabilization temperature, but distinctly higher than said intended working temperature, and at an oxygen pressure approximately equal to said stabilization pressure, until the resistance of said layer has reached a predetermined measured value; replacing said oxygen gas by a neutral gas and progressively cooling in a neutral atmosphere said thin metal layer having an adjusted resistance value.

2. The process of claim 1 wherein said neutral gas is argon.

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3. The process of claim 1 wherein the thickness of said layer of oxide formed during the oxidation step is adjusted as a function of the decrease in the thickness of said thin layer, said decrease being determined by means of the variation of resistance of said thin layer.

4. The process of claim 1 further comprising continuously measuring resistance of the thin layer resistors during the maintaining step.

5. The process of claim 1 further comprising continuously measuring resistance of one of a group of thin layer resistors during the maintaining step.

6. The process of claim 1 further comprising continuously measuring resistance of the thin layer resistors during the maintaining step, and automatically discontinuing heating upon resistance reaching a predetermined value.

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WILLIAM L. JARVIS, Primary Examiner

U.S. Cl. X.R.

117—62, 118; 148—6.3; 338—308

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,546,015

Dated Dec. 8, 1970

Inventor(s) Georges Francois Vulliez, Jean-Claude Georges He
Marquet

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

In the heading insert --assignors to Societe Alsacienne
de Constructions Atomiques de Telecommunications et
D'Electronique Alcatel--.

SIGNED AND
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Attest:

Edward M. Fletcher, Jr.

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Commissioner of Patents