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NITROGEN STABILIZED TITANIUM THIN FILM
RESISTOR AND METHOD OF MAKING SAME
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FIG. 1

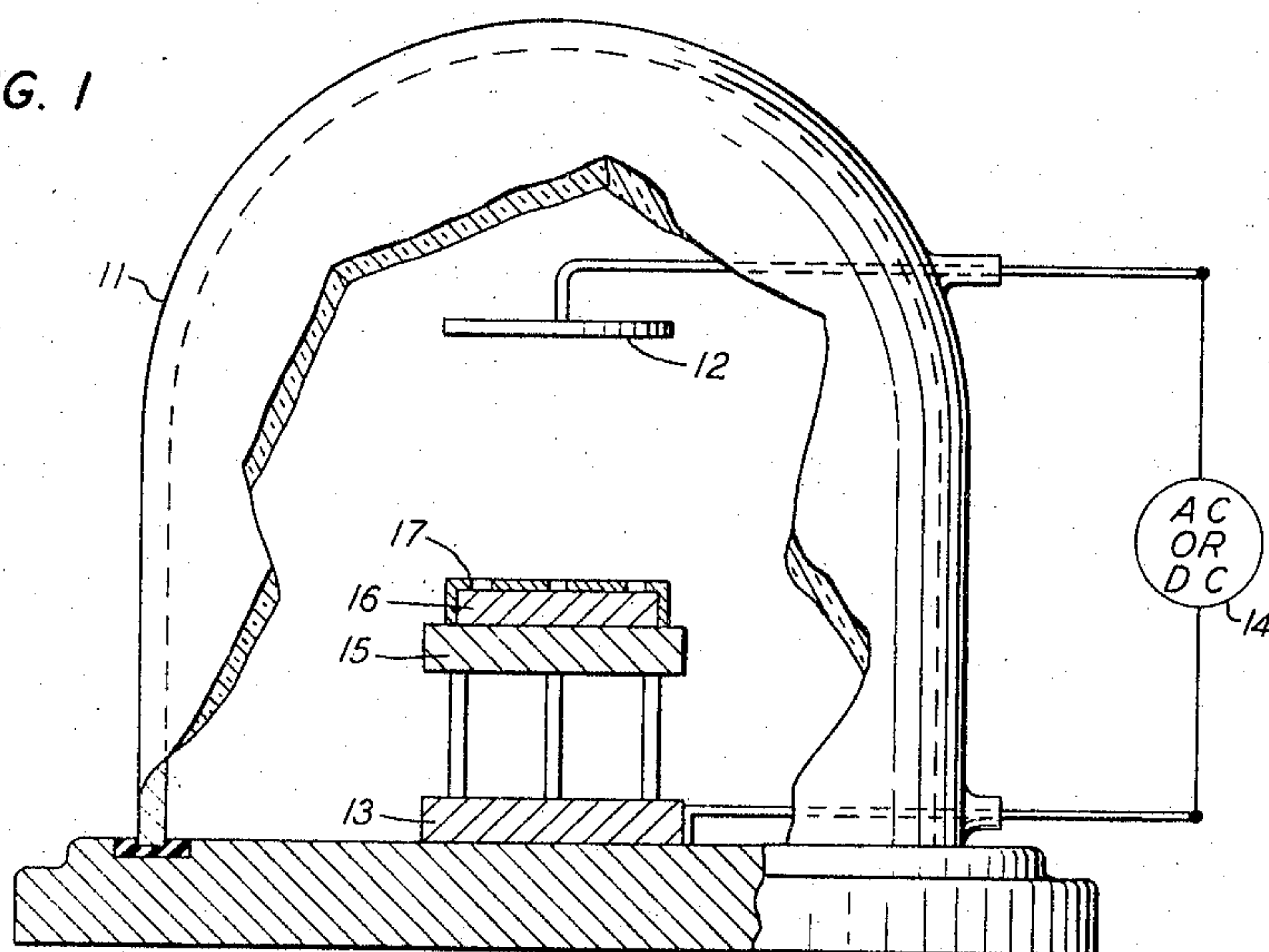
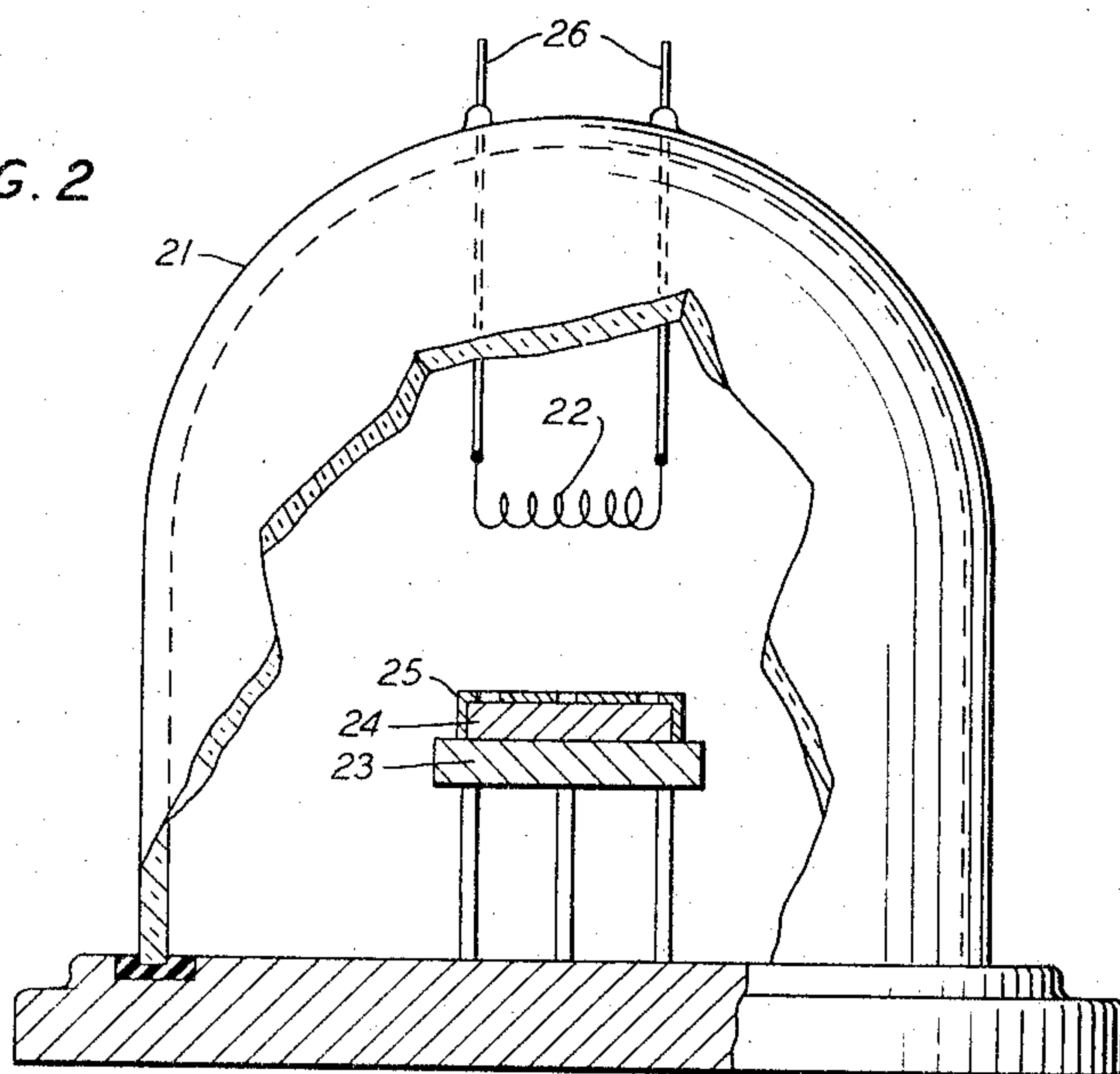


FIG. 2



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NITROGEN STABILIZED TITANIUM THIN FILM RESISTOR AND METHOD OF MAKING SAME

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5 Claims. (Cl. 338—308)

This application is a continuation-in-part of copending application Ser. No. 144,190, filed Oct. 10, 1961, now abandoned.

This invention relates to a technique for the fabrication of thin film nitrogen saturated titanium resistors.

In recent years, the most widely used procedure for the fabrication of printed circuit resistors has involved depositing a film forming metal by condensation techniques upon a substrate in a configuration such that the resistance of the deposited layer is less than that ultimately desired and, subsequently, anodizing the deposited film to convert a portion of the metal layer thickness to the corresponding oxide form, thereby increasing the resistance of the layer to a desired value.

Unfortunately, it was observed that freshly deposited films, particularly titanium, evidenced a certain degree of instability of resistance both at room and elevated temperatures, so restricting their use in certain device applications. It has been theorized that such variations in resistance were attributable, in part, to the growth of an oxide film by ambient oxidation of the deposited film and to annealing of the thin film structure, so suggesting the need for a stabilization step subsequent to deposition.

Further experimentation in thin film technology led to the discovery that stabilization of thin film resistors could be effected by thermal aging deposited films at temperatures within the range of 200–400° C. for time periods ranging from two to ten hours. However, it was determined that the appended stabilization step was not completely satisfactory with regard to titanium film resistors. Accordingly, it became evident to workers in the art that a radically different approach was necessary in titanium resistor technology in order to avoid the apparent impediment to the total exploitation of titanium thin film as resistive materials.

The next stage in the evolution of titanium resistor technology involved focusing attention upon titanium compounds. One of the earliest compositions examined in this connection was titanium nitride, a material found to evidence a lower resistivity than bulk titanium and an inordinately high temperature coefficient of resistance, so rendering it unacceptable as a resistor material for greater than 99 percent of the device applications contemplated. Accordingly, it was concluded by the vast majority of those working in the art that titanium nitride, per se, was of no interest in thin film resistor applications.

In accordance with the present invention, a novel departure from prior art techniques is made by heating a freshly deposited titanium film in a gaseous ambient consisting essentially of nitrogen at temperatures within the range of 200–375° C. for a time period within the range of one to three hours, thereby resulting in the formation of an opaque nitrogen-saturated titanium film evidencing the same crystallographic structure as bulk titanium. The resultant films have been found to manifest a lower negative temperature coefficient of resistance and a higher specific resistivity at the solubility limit of nitrogen than

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either pure titanium films or titanium nitride films. Further, it has been determined that thermal pre-aging of the described films at elevated temperatures results in a device evidencing a marked improvement in stability.

The invention will be more readily understood from the following detailed description, taken in conjunction with the accompanying drawing in which:

FIG. 1 is a front elevational view of an apparatus suitable for use in producing a film of metal by cathodic sputtering in accordance with the present invention; and

FIG. 2 is a front elevational view of an apparatus suitable for use in producing a film of metal by vacuum evaporation in accordance with the present invention.

It has been found that nitrogen saturated titanium films produced in accordance with the present invention are opaque over the entire range of thicknesses employed, 400 Å–1500 Å. (approximately one-twelfth to one-fourth wavelength).

Following the deposition technique, the deposited titanium film is heated in a tube furnace in the presence of free flowing pure nitrogen at temperatures within the range of approximately 200–375° C. for a time period of the order of one to three hours, so resulting in the formation of an opaque nitrogen saturated titanium film evidencing the crystallography structure of bulk titanium. It has been determined that temperatures appreciably below 200° C. are impractical due to the sluggish rate of saturation. The upper limit of 375° C. is not absolute and temperatures ranging as high as 400° C. may be employed. However, it has been found that temperatures appreciably beyond 450° result in the formation of transparent oxide layer due to preferential reaction of the titanium with oxygen, such layer being unacceptable for resistor purposes. The indicated limit of 375° C. is chosen as a preferred expedient, such preference being dictated by practical considerations of substrate sensitivity to heat.

A second illustrative example of this invention involves the production of a resistor employing vacuum evaporation techniques to produce the layer of titanium. The over-all process exclusive of the deposition step is essentially the same as that described in the first example.

Vacuum evaporation is generally conducted at extremely low pressures. An apparatus similar to that shown in FIG. 2 is conveniently employed for this step. The extent of the vacuum is dictated by consideration of the vapor pressure of the titanium. In conventional vacuum evaporation processes, it is generally considered that the vapor pressure of the metal to be evaporated should be at least ten times greater than the pressure to which the system is evacuated. For the evaporation of titanium, it has been determined that a pressure of approximately 3×10^{-3} microns of mercury is satisfactory.

The usual method of heating the metal to be evaporated is to position it in proximity to a filament which may be heated electrically. This is conveniently accomplished by using a tungsten filament in the shape of a coil, as shown in FIG. 2, and placing the titanium to be evaporated within the coil. The required temperature is obtained by controlling the magnitude of the current flowing through the filament. Vacuum chamber 21 is evacuated to the prescribed pressure and a current is passed through the tungsten filament 22. The filament gradually is heated, thereby causing the titanium, not shown in FIG. 2 to evaporate.

The considerations discussed above with respect to the thickness of the layer produced in the first example also apply here. The thickness of the deposit depends upon

the position of the substrate and the total amount of titanium evaporated. These factors are known in the art.

The thermal treatment subsequent to deposition is similar to that described below in the first example.

In the claims appended to this disclosure, the term "condensation" is used to describe the method by which the titanium layer is produced on the substrate. In the sense that "condensation" is descriptive of the formation of a more compact mass, this word is intended to include the formation of the titanium layer by either cathodic sputtering or vacuum evaporation techniques.

Several examples of the present invention are described in detail below. These examples and the two illustrations described above are included merely to aid in the understanding of the invention, and variations may be made by one skilled in the art without departing from the spirit and scope of the invention.

Example 1

This example describes the fabrication of four titanium resistors by cathodic sputtering in accordance with the present invention.

A cathodic sputtering apparatus similar to that shown in FIG. 1 was used to produce the titanium layer. The cathode consisted of a circular aluminum disc 4 inches in diameter which was covered on all sides with titanium foil of high purity. In the apparatus actually employed, the anode was grounded, the potential difference being obtained by making the cathode negative with respect to ground.

Four glass microscope slides, approximately 1 inch in width and 3 inches in length were used as the substrates. Gold terminals, 3/8 inch by 1/4 inch were silk screened on each longitudinal side of the substrate. The gold terminations were fired at 565° C. and had a final resistance of approximately 0.2 ohm per square. The terminated slides were then cleaned using the following procedure. The slides were first washed in a detergent, such as "Alconox," to remove large particles of dirt and grease. Next, there followed a tap water rinse, a ten minute boil in a 10 percent hydrogen peroxide solution, a distilled water rinse, a ten minute boil in distilled water, and storage in an oven maintained at 150° C. until ready for use.

The vacuum chamber was evacuated by means of a roughing pump and an oil diffusion pump to a pressure

Following the sputtering treatment, the resistance in ohmic per square, specific resistivity in microhm centimeters, and the temperature coefficient of resistance were measured. Next, the four metal film resistors were inserted into a tube furnace and heated in an atmosphere consisting essentially of free-flowing nitrogen for one hour at temperatures of 290°, 332° and 400°. The resultant films were found to be opaque in nature and evidenced the crystallographic structure of bulk titanium. The resistive device was completed by the attachment of two spaced electrical leads after which the properties were again determined. The results are set forth in Table I below.

Example 2

This example describes the production of two resistors in which titanium was evaporated onto a substrate to form the requisite metal layer.

An apparatus similar to that shown in FIG. 2 was employed, the filament being composed of a helical coil of four strands of tungsten wire. The substrates employed were microscope slides which were cleaned in a manner similar to that described in Example 1. After cleaning, the slides were placed approximately 5 inches from the tungsten filament and a mask placed on the slide. A highly purified titanium wire weighing between 20 and 100 milligrams was placed within the tungsten filament. The vacuum chamber was then evacuated to a pressure of approximately 2×10⁻⁶ microns of mercury. Current was next caused to flow through the tungsten filament, heating it to incandescence and thereby heating the titanium wire and causing it to evaporate. Evaporation was conducted for approximately 30 seconds, so producing titanium layers of approximately 418 and 538 Angstroms.

The evaporated layers were then examined to determine the electrical properties. Next, the two resistors were inserted into a tube furnace and heated in an atmosphere of free flowing nitrogen for time periods of one hour at a temperature of approximately 400° C. The films so prepared were opaque in nature and evidenced the crystallographic structure of bulk titanium. Spaced electrical leads were attached to the films and the properties again determined. To determine the stability of both the sputtered and evaporated films, aging was conducted by thermal treatment at 150° C. for 1000 hours. The results are set forth in the table below.

TABLE I

Example	Type of Film	F. T. in A.	Initial R in Ω/□	Spec. Res. in μΩ-cm.	TCR α in 10 ⁻⁶ /°C.	T° of heat treatment α in N ₂ , °C.	R in Ω/□ after heat Treat	TCR α in 10 ⁻⁶ /°C.	Spec. Res. in μΩ-cm.	Δ R% after 1,000 h. at 150° C.
1-----	Sputtered for 6 minutes.	450	54.15	244.0	+681	290	83.8	-82	377.0	1.92±0.12
2-----	Sputtered for 10 minutes.	750	26.90	202.0	+1,120	352	45.4	-54	340.0	1.05±0.29
3-----	Sputtered for 13 minutes.	975	17.83	174.0	+1,315	400	36.0	+16	351.0	0.55±0.18
4-----	Sputtered for 17 minutes.	1,275	12.90	164.0	+1,550	425	26.10	-20	332.0	0.62±0.30
5-----	Evaporated-----	418	27.50	115.00	3,550	400	91.50	-130	382.0	0.43±0.09
6-----	do-----	538	18.55	100.00	3,920	400	59.20	+62	318.0	0.25±0.11

F.T.=film thickness. Initial Resistance (R) in ohms per square. TCR=temperature coefficient of resistance.

of approximately 3×10⁻⁶ millimeters of mercury after a time period within the range of 45 to 60 minutes. After obtaining such pressure, argon at a dynamic pressure of 10 microns was allowed to enter the sputtering chamber.

The anode and cathode were spaced approximately 2.5 inches apart, the masked substrate being placed therebetween at a position immediately without Crooke's Dark Space. A D.C. voltage of approximately 5000 volts was impressed between cathode and anode.

Sputtering was conducted for time periods of 6, 10, 13 and 17 minutes, producing layers of approximately 450, 750, 875 and 1275 Angstroms, respectively.

An analysis of the data set forth in the table indicates that substantial improvement in the electrical properties occur as a result of the nitrogen saturation. Furthermore, the stability of the resistors so produced is vastly improved over those resistors not given the nitrogen treatment as seen by analysis of Table II below.

The devices upon which the data of Table II is based were prepared in accordance with the procedure of Examples 1 and 2 with the exception that no nitrogen treatment was given after deposition. Thermal treatment again was conducted at 150° C. for 354 hours for sputtered films and 650 hours for evaporated films.

TABLE II

Example	Type of Film	Initial R in $\mu\Omega$ -cm.	Spec. Res. in $\mu\Omega$ -cm. after aging	Δ R% after 354 hrs. at 150° C.
1-----	Sputtered for 10 min- utes, 1,000 A.	226.0	150.63	7.80
2-----	do-----	226.0	136.31	6.80
3-----	do-----	226.0	131.48	5.80
4-----	do-----	226.9	154.58	5.80
5-----	do-----	226.0	127.83	6.94
6-----	Evaporated, 600 A-----	102.0	80.89	5.82
7-----	do-----	102.0	77.03	3.30
8-----	do-----	102.0	78.65	3.44
9-----	do-----	102.0	85.47	6.97

The data of Table II clearly indicates that the resistors not given the nitrogen saturation treatment of the present invention were far less stable than those treated in nitrogen.

While the invention has been described in terms of cathodic sputtering and vacuum evaporation with a subsequent nitrogen saturation, it will be appreciated by those skilled in the art that the invention is not limited thereto and other techniques may be employed for saturating the titanium with nitrogen.

What is claimed is:

1. The method of fabricating an opaque nitrogen saturated titanium film resistor which comprises the steps of producing a thin layer of titanium having a thickness

ranging from 400 A. to 1500 A. on a substrate by condensation and heating said layer in a gaseous atmosphere consisting essentially of nitrogen at temperatures within the range of 200° to 375° C. for a time period within the range of one to five hours, thereby saturating said layer of titanium with nitrogen.

2. The method of claim 1 wherein said titanium layer is produced by cathodic sputtering.

3. The method of claim 1 in which the titanium layer is produced by vacuum evaporation.

4. The method of claim 1 wherein two spaced electrical leads are attached to said layer.

5. A thin film resistor including a substrate member, a nitrogen saturated opaque titanium film deposited thereon and a pair of spaced electrical leads attached to said film, said film having a thickness of 400 A. to 1500 A.

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