

Jan. 1, 1963

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3,071,522

LOW RESISTANCE CONTACT FOR SEMICONDUCTORS

Filed Oct. 30, 1958

3 Sheets-Sheet 1

FIG. 1

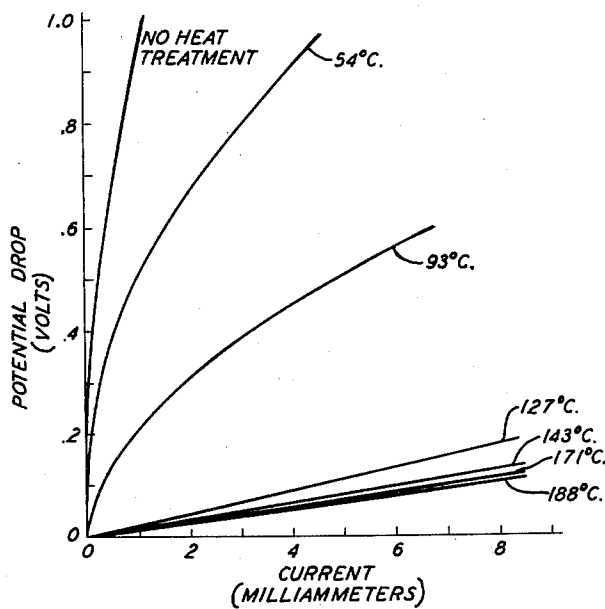
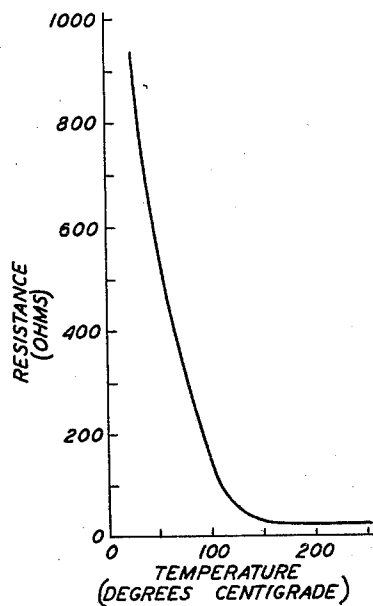


FIG. 2



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3 Sheets-Sheet 2

FIG. 3

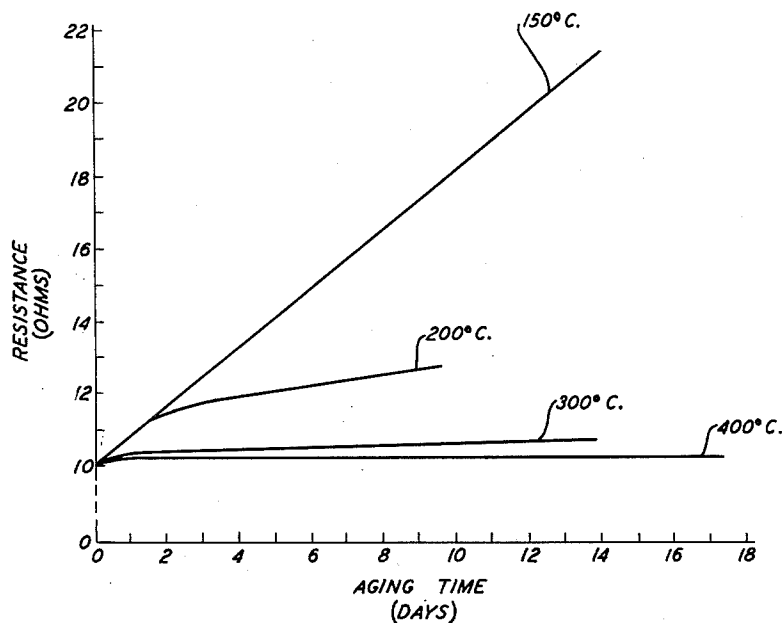
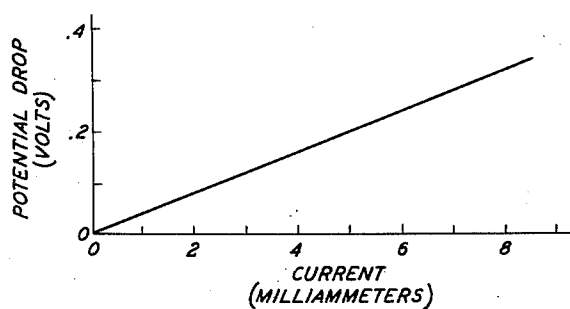


FIG. 4



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3 Sheets-Sheet 3

FIG. 5

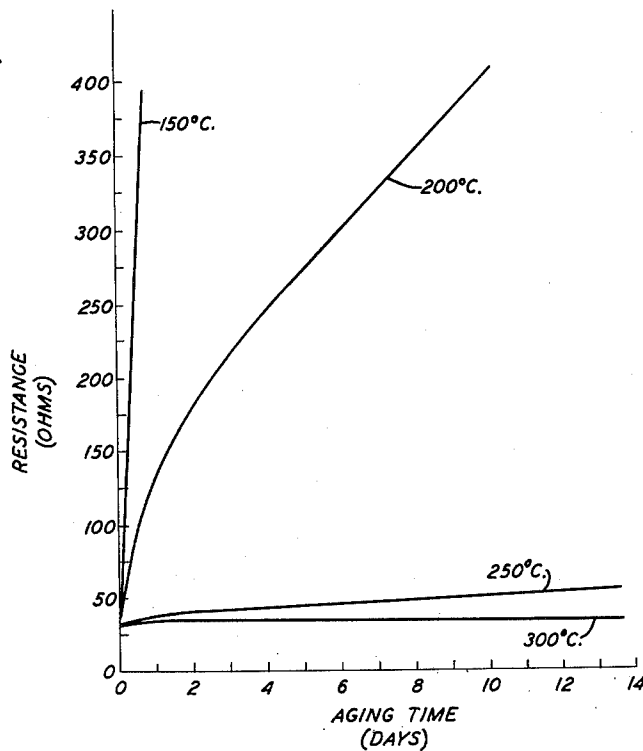
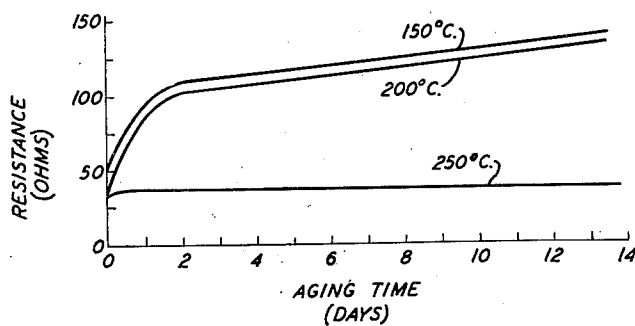


FIG. 6



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3,071,522 LOW RESISTANCE CONTACT FOR SEMI-CONDUCTORS

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7 Claims. (Cl. 204-37)

This invention relates to a method for producing stable, low-resistance, ohmic contacts to non-insulating surfaces.

There are presently a number of materials including semiconducting ceramics, semiconducting oxides and ferrites whose unique electrical properties make them suitable for a wide variety of applications such as thermistors, varistors, transducers and pressure sensitive devices such as acoustic transducers. Because of the increasing importance of these devices, there is a continuing search for a simple method by which stable, low resistance, ohmic metal contacts may be made to the non-insulating surfaces involved.

The term "ohmic" contact is intended to denote a contact whose electrical resistance is substantially independent of both the polarity and magnitude of the voltage impressed across it, and also independent of the magnitude of the current passing through it. A "stable" contact is one whose resistance remains substantially unchanged upon aging.

In general, many prior art techniques have not proven to be suitable for the production of stable, low-resistance, ohmic contacts to the materials described above. The crux of the problem of producing such contacts is the wide disparity in the properties of the substrate and the metal contact material. Thus, for example, the predominance of oxygen linkages in a ceramic material renders the making of a low-resistance metal contact to the surface thereof highly difficult.

In the instance of n-type semiconducting materials, such as lanthanum-doped barium titanate, there is another factor which tends to hinder the production of suitable electrical contacts. The presence of a high concentration of free electrons in the surface of such materials is believed to attract oxygen molecules from the atmosphere which become chemisorbed and form a barrier layer. The presence of this barrier layer interferes with the production of a stable low resistance contact to the surface of such materials.

In accordance with the present invention, stable, low-resistance, ohmic contacts are produced to non-insulating surfaces. A variety of metals, including gold, copper and nickel are suitable for use in conjunction with the inventive method. High melting point alloys may be used to make electrical connections to contacts of such metals and, accordingly, devices so produced may be operated at relatively high temperatures.

The method of the present invention consists essentially of two steps. In the first step, a metal film is deposited on the surface under certain conditions, discussed in detail below. The second step of the method consists of heat treating the metal film and the substrate at an elevated temperature of a prescribed period of time. Upon the completion of the above two steps, a low-resistance metal contact is produced which is stable and ohmic in character.

The invention will be better understood from the following detailed description taken in conjunction with the drawings in which:

FIG. 1 is a graph on coordinates of potential drop versus current showing the change in potential drop across contacts of this invention as a function of the current passing therethrough for various heat treating temperatures;

FIG. 2 is a graph on coordinates of resistance versus temperature depicting the change in electrical resistance of contacts of this invention as a function of the temperature at which it is heat treated for a constant current;

FIG. 3 is a graph on coordinates of resistance versus aging time depicting the change in resistance of contacts of this invention as a function of aging time for various heat treating temperatures;

FIG. 4 is a graph on coordinates of potential drop versus current depicting the potential drop across contacts of this invention as a function of the current passing therethrough after aging;

FIG. 5 is a graph on coordinates of resistance versus aging time depicting the change in resistance of contacts of this invention as a function of aging time for various heat treating temperatures; and

FIG. 6 is a graph on coordinates of resistance versus aging time depicting the change in resistance of contacts of this invention as a function of aging time for various heat treating temperatures.

With reference now more particularly to the drawings:

FIG. 1 is a group of related curves depicting the effect of heat treatment temperature on the voltage-current relationship of a lanthanum-doped barium titanate ceramic on which two nickel contacts were produced in accordance with this invention. The curves of FIG. 1 were produced as follows:

A disc of lanthanum-doped n-type barium titanate 400 mils in diameter and 125 mils thick was fabricated in the customary manner. Nickel contacts were produced on the opposite broad faces of the ceramic disc by the electroless plating process (see National Bureau of Standards, Circular No. 529 (1953), page 25, and Metal Finishing, August 1955, page 59).

The electroless process, as practiced to produce the contacts of FIG. 1, consisted of several steps. For optimum results the surfaces upon which the nickel was to be deposited were first lapped using a fine abrasive. This was accomplished using No. 600 silicon carbide powder.

After cleaning the lapped surfaces with distilled water, they were contacted for approximately one minute with an aqueous stannous chloride solution maintained at 25° C. The solution comprised 200 grams of stannous chloride (SnCl_2), 50 cubic centimeters of concentrated hydrochloric acid (37-38 percent by weight) and water to make one liter of solution.

Following a water rinse, the surfaces were contacted for approximately one minute with an aqueous palladium chloride solution maintained at approximately 25° C. The solution comprised 0.1 gram of palladium chloride (PdCl_2), one cubic centimeter of concentrated hydrochloric acid (37-38 percent by weight) and water to make one liter of solution. This treatment produced a thin film of metallic palladium on the exposed surfaces.

After thorough water rinsing, the disc was then immersed in an electroless nickel plating solution for approximately 3 minutes. The solution, which was maintained at approximately 95° C., was made up as follows:

	Grams
Nickel chloride ($\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$)	30
Sodium hypophosphite ($\text{NaH}_2\text{PO}_2 \cdot \text{H}_2\text{O}$)	10
Ammonium citrate ($(\text{NH}_4)_2(\text{HC}_6\text{H}_5\text{O}_7)$)	65
Ammonium chloride (NH_4Cl)	50
Water to make 1 liter.	
Ammonium hydroxide to change color of solution from green to blue.	

A variable electrical potential source was then connected across the nickel-plated disc. Means for measuring the current flowing through the disc was also intro-

duced into the circuit. In this manner, the current flowing through the disc and contacts was determined for various impressed voltages. These data were plotted on the coordinates in FIG. 1, the resulting curves being marked "No Heat Treatment."

The disc was then heated to approximately 54° C. for a period of 10 minutes. After cooling to room temperature, voltage-current data were obtained in the manner described above. These data were plotted and the resulting curve was marked "54° C." to denote that the measurements were made after heat treating the disc to this temperature.

The other curves in FIG. 1 were obtained by repetition of the above-described procedures at the temperatures noted.

Examination of the curves of FIG. 1 reveals that the disc initially has a non-linear voltage-current relationship which approaches linearity as the heat treating temperature is increased. Thus, after heat treatment at a temperature of approximately 171° C., the current-voltage relationship is substantially linear, indicating a constant resistance for the values of currents and voltages indicated.

FIG. 2 is a plot of the sum of resistances of the disc and the two nickel contacts as a function of heat treating temperature. The curve in FIG. 2 was obtained from the curves of FIG. 1 by plotting the potential drop across the disc at 1 milliamper current flow for the various heat treating temperatures. The units of resistance in FIG. 2 were obtained by multiplying the potential drop in volts by 1000. It is seen that the resistance decreases from approximately 950 ohms to an essentially constant value of approximately 25 ohms.

The n-type lanthanum-doped barium titanate of which the disc was composed is known to have a positive temperature coefficient of resistance over a limited range of temperatures. That is to say, in this limited temperature range, its resistance increases with increasing temperature. However, at constant temperature, its resistance is unaffected by changes in the magnitude of the impressed voltage or the magnitude of the current flow. It is also known that heat treating at temperatures low relative to its sintering temperature has essentially no effect on the resistance of the titanate of concern. Accordingly, the reduction in the overall resistance indicated in FIG. 2 must be attributed to a change in the character of the nickel contacts. Likewise, the change in character of the resistance from non-ohmic to ohmic is also due to a change in the character of the contacts.

FIG. 3 illustrates the effect of the temperature of the heat treatment on the stability of contacts of this invention. Four nickel-plated discs were prepared and heat treated for 30 minutes at the temperatures noted in FIG. 3. Prior to heat treating, the nickel contacts were coated with gold to prevent oxidation of the nickel during the heat treatment. The current-voltage relationship of each of the discs was determined after the heat treatment. From these data, the resistance of each of the discs was calculated and this information was then plotted in FIG. 3 on the ordinate which represents zero aging time. The discs were then aged at approximately 80° C., the discs being maintained at such temperature by Joule heating. The above-described measurements were repeated at regular intervals and the resultant data plotted accordingly. As illustrated in FIG. 3, a heat treatment temperature of approximately 400° C. is required to produce a stable contact.

Although the data in FIG. 3 were obtained using heat treatment times of 30 minutes duration, it has been determined that placing a nickel-coated disc in an oven maintained at 400° C. for a five-minute period imparts a stability substantially equal to that obtained for a heating period of thirty minutes. Since a period of a few minutes is required for the disc to attain the temperature of the oven, 400° C., it is seen that only a brief treat-

ment at 400° C. is necessary to stabilize the contacts of this invention.

It was further determined that heat treating a nickel-coated disc at a temperature of 200° C. for a period of twenty-four hours did not produce any substantial change in the aging characteristics from those in FIG. 3. Thus, it is not possible to compensate for a deficiency in the required heat treatment temperature by employing longer heat treating periods.

In view of the foregoing, it is considered that there is a minimum heat treatment temperature which must be attained in order to achieve a stable contact of this invention. The heat treatment time is not a critical parameter, the only requirement being that the contact and substrate bear the minimum heat treatment temperature for a short period of time. From the data in FIG. 3, it is seen that this minimum temperature for nickel is approximately 400° C.

FIG. 4 depicts the voltage-current relationship for a nickel-plated disc produced in accordance with this invention which was heat treated at 400° C. for approximately 30 minutes and aged for approximately 16 days at 80° C. As shown in FIG. 4, the resistance of the aged disc remained ohmic in character.

FIG. 5 is a graph showing the effect of heat treatment temperature on the stability of gold contacts produced in accordance with this invention. The discs whose characteristics are depicted in FIG. 5 were fabricated in the following manner. Four n-type lanthanum-doped barium titanate discs 400 mils in diameter and 125 mils thick were treated in the manner described above for the production of the nickel contacts up to the point of immersing the discs in the electroless nickel plating solution. At this stage in the procedure, the masked discs were immersed in a conventional gold cyanide plating solution, and a layer of gold was electroplated on the opposing broad faces of each of the discs.

The four discs so produced were then heat treated for approximately 10 minutes at temperatures of 150° C., 200° C., 250° C. and 300° C., respectively. The discs were then aged at 80° C. and the voltage-current relationships of the discs were measured at regular intervals of time. FIG. 5 is the result of plotting the resistances calculated from these measurements as a function of the aging time in days. It is seen that the minimum heat treatment temperature for gold contacts produced in accordance with this invention is approximately 300° C.

FIG. 6 is a group of related curves depicting the effect of heat treatment temperature on the stability of copper contacts produced in accordance with the present invention. The copper contacts were produced in a manner similar to that described above for the gold contacts except that copper cyanide was used as the plating solution. The copper-plated discs were heat treated for approximately 10 minutes at the respective temperatures indicated in FIG. 6. The discs were then aged at 80° C. and voltage-current measurements made at regular intervals of time. FIG. 6 is the result of plotting the resistances calculated from these measurements as a function of the aging time in days. From the data in FIG. 6, it is seen that the minimum heat treatment temperature for copper contacts is approximately 250° C.

Metal contacts which have been found to be susceptible to improvement and stabilization by heat treatment in accordance with this invention are those produced in the presence of nascent hydrogen.

As indicated by FIGS. 5 and 6, stable, low-resistance, ohmic contacts are produced in accordance with this invention from electroplated metal coatings. FIGS. 5 and 6, which represent contacts of this invention consisting of gold and copper, respectively, indicate results comparable with those achieved by the electroless process. It has also been determined that nickel contacts produced by electroplating in accordance with this invention are possessed of characteristics which permit their stabilization in a man-

ner similar to those produced by the electroless process. Where the contacts of this invention are produced by electroplating, the nascent hydrogen is produced by the electrolytic reduction of hydrogen ions present in the plating solution.

As is well known, most oxidation-reduction reactions may be carried out electrolytically. The usual electrolytic process includes at least two such reactions, termed half-cell reactions, at least one of which proceeds at the anode, and at least one at the cathode. Each of these half-cell reactions is classified according to the theoretical potential required to cause it to proceed, this potential being termed the half-cell potential. (See Glasstone, "Introduction to Electrochemistry," pages 231, 488, New York, D. Van Nostrand Co., Inc., 1942.) In the classification referred to above, the hydrogen half-cell potential is used as the basis, and is given the value of zero. This hydrogen half-cell reaction is generally termed the standard hydrogen half-cell.

If the half-cell reaction which represents the formation of the metal plate has a more negative theoretical half-cell potential than the standard hydrogen half-cell, nascent hydrogen will be produced as a by-product of such a plating process. Accordingly, the requirements of this aspect of the invention are met if the half-cell reaction which represents the formation of the metal plate has a theoretical potential, which is negative with respect to the standard hydrogen half-cell. It is preferable to choose a plating half-cell reaction whose theoretical potential is at least minus one volt with respect to the standard hydrogen half-cell. This latter condition is achieved by the use of a plating solution consisting of the cyanide of the metal to be plated. The use of the cyanide complexes the metal ion and necessitates the use of a more negative potential to produce a plate.

In the electroless process described above, nascent hydrogen is present as a by-product of the process. (See Proc. Amer. Electroplater's Society, 33rd Annual Meeting, page 23, 1946.)

In the description given above in conjunction with FIGS. 5 and 6, it was noted that the ceramic surfaces were pretreated by successively contacting the surface with stannous chloride and palladium chloride solutions. It has been determined that such a procedure shortens the period of time necessary to produce a plate. However, contacts may be produced in accordance with this invention by introducing the ceramic directly into the electroplating solution without the above-mentioned pretreatment.

The manner in which the heat treatment step of this invention produces a change in the character of the metal contacts is not known. It has been determined that silver is not suitable for use in this invention. Heat treatment of silver contacts formed by electroplating from a silver cyanide solution produced no appreciable change in the character of the contacts. Thus, although the existence of a minimum heat treatment temperature, the value of which appears to be dependent upon the particular metal used, suggests that a chemical reaction may be responsible for the marked change in characteristics of the contact which result upon heat treatment, there does not appear to be a logical basis for predicting which metals are suitable and which are not.

The thickness of the metal contacts is not critical, thicknesses in the range of 0.05 mil to 0.15 mil having been

found suitable. Depending on the particular application, the contact may need sufficient thickness to permit the soldering of a lead wire thereto. Contacts one-tenth of a mil in thickness have been found to meet this requirement.

Contacts thicker than .15 mil may be used but do not afford any substantial advantage.

Although the detailed description of this invention set forth above was concerned with a specific material, n-type barium titanate, it is to be understood that this invention is applicable to all types of non-insulating materials including semiconductors, ceramics, oxides and combinations thereof, such as ferrite materials. It is noted that ohmic contacts in accordance with this invention have been applied to materials such as single crystals of titanium dioxide, single crystals of p-type binary alloy semiconductors such as Bi_2Te_3 , and p-type ternary alloy semiconductors such as AgSbTe_2 and AgBiTe_2 .

It is to be appreciated that the examples described above are intended merely as illustrative of the present invention. Variations may be made in the inventive method as above described by one skilled in the art without departing from the spirit and scope of the invention.

What is claimed is:

1. The method of producing a stable, ohmic, low resistance metal contact to a semiconducting refractory oxygen-bearing substrate comprising the steps of depositing a layer comprising at least one metal selected from the group consisting of nickel, gold and copper on said surface in the presence of nascent hydrogen, and heating said surface and said layer to an elevated temperature sufficient to form a stable ohmic low resistance contact said nickel being heated to a temperature of at least approximately 400°C ., said gold being heated to a temperature of at least approximately 300°C ., and said copper being heated to a temperature of at least approximately 250°C .

2. The method of claim 1 in which the said metal is nickel deposited by the electroless plating process.

3. The method of claim 1 in which the semiconducting refractory oxygen-bearing substrate is a ceramic material.

4. The method of claim 1 in which said metal layer is deposited electrochemically from a plating solution, the theoretical half-cell potential of the plating reaction from the said plating solution being negative with respect to the standard hydrogen electrode.

5. The method of claim 4 in which the said metal layer is gold.

6. The method of claim 4 in which the said metal layer is nickel.

7. The method of claim 4 in which the said metal layer is copper.

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