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M. KAHN

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ELECTRICAL DEVICE HAVING OHMIC OR LOW LOSS CONTACTS

Original Filed Sept. 23, 1969

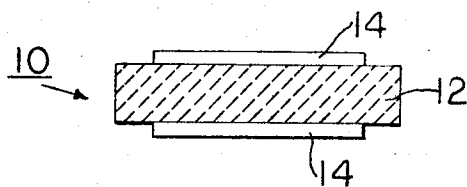


FIG. 1

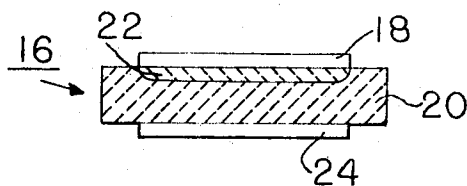


FIG. 2

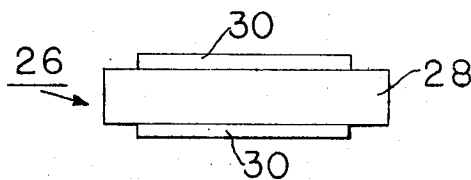


FIG. 3

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ELECTRICAL DEVICE HAVING OHMIC OR LOW LOSS CONTACTS

Manfred Kahn, Williamstown, Mass., assignor to Sprague Electric Company, North Adams, Mass.

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5 Claims

ABSTRACT OF THE DISCLOSURE

An electrical device employs an inorganic substrate of the type having a highly electronegative element at least on the surface thereof. The substrate is selected from the group consisting of an insulator and a semi-conductor. In ohmic or low loss contact with said substrate is at least one electrode consisting essentially of a mixture of (1) a metal selected from a first group consisting of the platinum group metals, gold, silver and mixtures thereof and (2) a metal in in-situ oxidized form with at least some of the electronegative element of said substrate, said metal being at least one selected from a second group consisting of calcium, magnesium, barium, strontium, zinc, tin, vanadium, nickel, indium, titanium and chromium.

This is a division of application Ser. No. 860,343, filed Sept. 23, 1969, now abandoned.

BACKGROUND OF THE INVENTION

The present invention is concerned with ohmic or low loss contacts to inorganic bodies.

It is known that when certain commonly used electrode materials are applied to semiconducting oxide bodies, the D.C. resistances are orders of magnitude larger than the true resistances of the bodies. These excess resistances are usually voltage dependent. High contact resistances at the electrode interfaces are deemed responsible for this condition and it is to a great extent the cause for unstable performance in such electrical components.

There is evidence that oxidation or adsorbed oxygen at least on the surfaces of semiconducting ceramics is responsible for some of the high series resistance. In addition, the bond made to ceramics by conventional high firing glassy electrode frits destroys the stoichiometry of the ceramic at, and under, the surface and thereby creates another insulating layer of uncertain properties. The art would be significantly advanced if a means could be devised to eliminate these problems.

It is an object of the invention to present a novel ohmic or low loss contact to an insulator or semiconductor body.

It is another object to provide such a contact that is stable over a comparatively wide voltage range.

Yet another object is to present a novel process for forming such a contact that is simple, easy to implement and economical.

It is still another object of the invention to provide such a contact that is adherent and that is easily solderable.

These and other objects will become obvious to those skilled in the art by the following description when considered in relation to the accompanying drawing of which:

FIG. 1 is a side view of a section of a thermistor having electrodes in ohmic contact thereto.

FIG. 2 is a side view of a section of a capacitor having at least one electrode in ohmic contact thereto.

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FIG. 3 is a side view of another capacitor having two electrodes of the present invention in low loss contact thereto.

SUMMARY OF THE INVENTION

The present invention is concerned with an electrical device having an inorganic substrate of the type having on the surface thereof a strongly electronegative element. This substrate can be either an insulator or a semiconductor. In ohmic or low loss contact with said substrate is at least one electrode consisting essentially of a mixture of (1) a metal selected from a first group consisting of the platinum group metals, gold, silver and mixtures thereof and (2) a metal in in-situ oxidized form with at least some of the electronegative element, said metal being at least one selected from a second group consisting of calcium, magnesium, strontium, zinc, tin, vanadium, titanium, barium, indium, nickel and chromium.

The invention is also concerned with a method of preparing an electrical device having at least one electrode in ohmic or low loss contact with a substrate thereof. Depending upon the desired character of the ultimate device, either an insulator or a semiconductor is chosen as one of the starting materials. At least the surface of this material is a surface having thereon a strongly electronegative element. By this is meant that, for example, either oxygen is part of a thin oxide on the surface of the substrate, e.g. SiO_2 on the surface of silicon, or excess nonstoichiometric oxygens as can be adsorbed on the surface of BaTiO_3 due to the lattice discontinuities at the surface of the substrate.

To such a surface is applied a mixture of (1) a metal selected from a first group consisting of the platinum group metals, gold, silver and mixtures thereof; and (2) at least one metal selected from a second group consisting of calcium, magnesium, barium, strontium, zinc, tin, vanadium, nickel, indium, titanium and chromium. The applied mixture and the substrate are subjected to a temperature between about 1000-2500° F. for a time sufficient to cause oxidation of at least some of the second group metal by at least some of the electronegative element. This process results in the formation of an ohmic or low loss contact to said substrate.

The process of the present invention contemplates applying the metal mixture by any one of several different techniques. By one technique, the metals are applied as a mixture of said first group metal in powdered form and said second group metal in the form of a metalorganic compound of the formula MZ_x , wherein M is said second group metal; Z is R, OR, SR or OCOR; R is a C_1 - C_{20} organic group and x is 2-4. The mixture and the substrate is then subjected to a temperature between about 1000-2500° F. for a time sufficient to decompose said metalorganic compound and effect oxidation of at least some of its metal by at least some of the highly electronegative element of said substrate.

By another technique, the mixture of metals is applied to the substrate by the simultaneous evaporation of said metals under low pressure conditions, e.g. 10^{-3} torr or less, followed by firing the mixture and substrate to the above noted temperature.

The electrodes of the present invention may be utilized with any electrical component, e.g. capacitors, resistors, thyristors, thermistors, microcircuits, transistors, diodes, varistors, etc.

One capacitor utilizing the contact of the present invention employs a ceramic titanate body formed of comparatively large grains, e.g. 10-300 microns. The ceramic has

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two regions: a reduced, semiconducting region and a dielectric, insulating region. One electrode, as defined above, is in ohmic contact with said semiconducting region and a more conventional glass frit-metal containing electrode is in contact with said dielectric region.

BRIEF DESCRIPTION OF THE DRAWING

FIG. 1 of the drawing shows a thermistor 10 having a semiconducting ceramic body 12 with electrodes 14 of the present invention in ohmic contact thereto.

FIG. 2 of the drawing shows a capacitor 16 having a semiconducting ceramic body 20 with a thin layer 22 of nonconducting ceramic disposed between body 20 and a metallic electrode 18. Making ohmic contact with ceramic body 20 is electrode 24 of the present invention.

FIG. 3 shows a ceramic capacitor 26 having a dielectric ceramic body 28 with electrodes 30 of the present invention in contact thereto.

DETAILED DESCRIPTION OF THE INVENTION

While not intending to be bound by any particular theory of action, it is believed that the reason excellent ohmic or low loss contacts can be obtained by the technique of the present invention is because of the inclusion in the electrode material of a metal having a high oxidation energy. The inorganic substrate, be it an insulator or a semiconductor, has oxygen in or on the surface thereof. This is because either the material per se is an oxide or it has a loosely bound or adsorbed oxygen on the surface thereof. This oxygen or oxide can be combined or reacted with, or reduced by a metal having a high oxidation energy during the firing of the electrode composition. This intimate combination of the electrode material with the surface oxygen provides an adherent bond and eliminates electrical losses between the electrode and the ceramic.

It is to be understood that while oxygen is probably the common agent preventing a good contact, it is not the only such agent. For example, chlorides and sulfides on the surface of the substrate may inhibit good contact formation. Thus, in the broad sense, any substrate having on the surface thereof strongly electronegative elements i.e. those over about 2.2 on the Electronegativity Scale (after Pauling) I, Se, C, S, Br, N, O and F will tend to inhibit the formation of a good contact. Therefore, as employed herein, the terms "oxidation" or "oxidized form" and the like, refer to oxidation in its broader sense of involving the loss of electrons and not merely combination with oxygen.

Example I

A thermistor having ohmic contacts was formed as follows: a semiconducting ceramic disc, ¼ inch in diameter and 20 mils thick was formed from BaTiO_3 , doped with 0.1 weight percent Nb_2O_5 , by mixing the niobium with powdered barium titanate and firing the unit to maturity. An electrode composition was formulated from 25 grams of powdered palladium and 20 grams of zinc octanoate (containing 13.7% zinc by weight) mixed with 1.1 milliliters of terpineol. Employing this composite paste, electrode patterns having a fired diameter of 200 mils, were applied to opposite surfaces of the disc. The unit was fired at a temperature of 2200° F. for a period of ten minutes.

Testing the completed unit revealed a resistance of 80 ohms which changed less than 20% when measured with applied voltages between 10 millivolts and 7 volts. This resistance was at least ten times lower and the linear range at least three times larger than that obtained from prior art electrode compositions on identical ceramics.

Example II

By way of comparison, a ceramic disc of the same composition as Example I, formed under the same conditions, had applied to opposite surfaces thereof an electrode com-

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position of 50 percent by weight of palladium powder in terpineol. Electrode patterns of the same dimensions as in Example I were applied and the unit fired at 2200° F. for ten minutes.

Testing the completed unit revealed a resistance of about 800 ohms which changed about 20% when measured with applied voltages between 10 millivolts and 1 volt. This indicates that the electrodes were not in ohmic contact with the ceramic.

Example III

A ceramic capacitor is formed as follows: a ceramic disc is prepared from barium titanate powder. The disc is fired to maturity at a temperature of 2550° F. for a period of about 15 minutes. During this firing, grains 10 to 300 microns large grow in the ceramic. The fired disc is 20 mils thick, and ½ inch in diameter. This unit is reduced in hydrogen at 2420° F. for about 3 hours to impart to the ceramic semiconducting characteristics throughout. An electrode composite is formulated from 25 grams of ultra-fine platinum powder and 9.5 grams of vanadium acetylacetonate (containing 21% V by weight) dissolved in 30 milliliters of isooctyl alcohol. An electrode pattern of this material, having a fired diameter of 450 mils, is applied to one side of the ceramic disc. The unit is fired in an atmosphere of nitrogen at a temperature of 1000° F. for a period of about ten minutes.

Testing the character of the electrode contact at this stage, using an identical unit but one having a split Pd-V electrode will reveal a resistance of 100 ohms which will change less than 20% when measured with applied voltages between 10 millivolts and 6 volts. This indicates an ohmic contact to the ceramic.

The capacitor is completed by applying a silver paste containing about 10% by weight of glass frit to the opposite side of the unit and firing it in air at a temperature of 1450° F. for a period of about ten minutes. During this firing the glass frit in the silver paste reacts with the ceramic and forms a dielectric reaction zone immediately adjacent to the silver in the surface region of the ceramic see 22 of FIG. 2 of the drawing. Because of the high temperature at which the ceramic is reduced, the silver firing treatment does not lower the conductivity of the ceramic surface that is not exposed to the frit and the silver, so that the ohmic contact to the first electrode is maintained. The resulting capacitor has twice the capacitance as that in conventional manufacture, where glass frit bearing electrode paints are applied to both sides of the disc.

Example IV

Another capacitor is formed as follows: a barium titanate containing ceramic disc ½ inch in diameter and 20 mils thick is fired in an oxidizing atmosphere so as to have dielectric properties. An electrode composite is formulated from 25 grams of powdered palladium and 13.1 grams of dibutyl tin dilaurate (containing 21% tin by weight) dissolved in 5.18 grams ethylcellulose. Employing this composite paste, electrode patterns having a fired diameter of 450 mils are applied to opposite surfaces of the fired disc. These electrodes are fired on at a temperature of 2450° F. The capacitor will have a dissipation factor of approximately 0.8%. Utilizing an identical disc but employing a commercial glass frit-containing silver electrode paint, the resulting capacitor will have a dissipation factor of over 1%.

Example V

This example illustrates the process of simultaneously evaporatively depositing a mixture of contemplated metals on a semiconductive substrate followed by firing the deposited film to the substrate.

A silicon bar, 1 cm. long, 0.1 cm. square and having a resistance of 10 ohms, said bar having a thin SiO_2 film thereon, is suspended, one end facing down, in a chamber evacuated to a pressure of 10^{-5} torr. Two separate evapo-

ration crucibles with individual heater means are positioned beneath the suspended bar. A quantity of powdered gold is placed in one crucible and a quantity of powdered chromium is placed in the other. A shielding means is placed over the silicon bar and the heater means are operated to bring the temperature of the chromium to 1615° C. and the gold to about 1500° C. The chromium temperature is adjusted so as to achieve in the deposited layer a ratio of 3 parts gold to 1 part chromium. At this point the shielding means is removed to expose the end of the silicon bar facing the crucibles and both metals are evaporatively deposited thereon for 45 seconds. This procedure is repeated for the other end of the silicon bar. The unit is removed and subjected to a heat treatment of 1000° F. for about ten seconds.

Resistance measurements will reveal that this unit has less than 11 ohms, with the resistance changing less than 20% over the range of applied voltages of from 1 millivolt to 1 volt.

By way of comparison, a unit prepared in the same manner as the foregoing example, except that only gold is evaporatively applied to each end of the silicon bar, will exhibit a resistance of about 100 ohms and its resistance will vary greatly with applied voltage.

While the foregoing example shows simultaneous deposition by evaporative techniques, other means of deposit such as, sputtering, deposition of reduced metal under nonoxidizing conditions, etc., may be employed. The invention also contemplates using the present technique to make contact to a metal, e.g. aluminum, having a surface layer of oxide.

While Example IV is directed to a simple two plate ceramic capacitor, the electrodes of the present invention find excellent utility in the monolithic type ceramic capacitor, where a plurality of layered electrodes are fired in a ceramic body. The structure of this type capacitor is well-known to one skilled in the art. In addition to monolithic multilayer capacitors, the present concept contemplates other multilayer devices, for example, multilayer resistors.

The broad concept of the invention can be practiced by employing any of the metals of the second group intimately mixed with a large proportion of a metal from the first group recited above. For the case of metalorganic compounds, it is preferred that a vehicle be chosen which is a solvent for the metal compound. It should be understood, however, that vehicles which only disperse or partially dissolve the compound can be employed to attain the objects of the invention. Examples of contemplated metalorganic compounds with an appropriate vehicle therefor, in addition to those of the specific examples, are: calcium propionate in isooctyl alcohol; magnesium stearate in dibutylphthalate; strontium oleate in castor oil; dibutyl tin dilaurate in terpeneol; tetrabutyltitanate in butyl alcohol; and chromium tertiarybutylbenzoate in eugenol.

In accordance with the above recited general formula for the metalorganic compounds, they can be any of the recited metals in organic combination. The metal may be directly linked to carbon in the compound e.g. metal alkyls, or it may be linked, through oxygen or sulfur, to organic groups, e.g. metal carboxylates, alcoholates and phenates, and their sulfur counterparts. The organic group of the compound can be a straight, branched chain or cyclic group. Since many of the metalorganic compounds are water soluble, particularly salts of carboxylic acids, the solvent of the composite can be water.

Concerning the ratio of proportions in the fired electrode mixture of the several constituents, the metal of the first group, that is the platinum group, etc., should be present in from 50-99% by weight of the electrode, and the metal of the second group, i.e. calcium, etc., should be present in from 1-50% by weight. The vehicle to be employed in preparing the composite can be present in the composite in widely varying proportions depending

upon the working consistency desired. Optimum proportions can be readily determined by one skilled in the art.

The inorganic body can be any of the commonly employed semiconducting or insulating materials used in electrical devices and includes, ceramics broadly, e.g. oxides, titanates, zirconates, glass, etc.; natural semiconductors, e.g. silicon, germanium, cadmium sulfide, gallium arsenide, etc.; or materials in which semiconductivity is induced by defects, i.e. by non-stoichiometry of the lattice or valence compensation as a result of different valence solutes.

Where a non-ohmic contact electrode is to be employed in conjunction with the electrode of the present invention, as in Example III, it can be any glass frit-containing prior art electrode, using silver, gold, platinum, etc. as the conductor.

Since there are a number of possible mechanisms by which the contacts of this invention can obtain a linear and low resistance, the constitution of the ohmic contact cannot be defined with certitude. Under the circumstances, the ohmic contact is best defined by reference to the essential starting materials and the fact that the metal of the second group is in in-situ oxidized form with the electronegative element on the surface of the substrate.

Use herein of the phrase "in ohmic contact" is with recognition that the contact has a finite resistance. This resistance is ohmic in that the ratio of voltage over current is fixed. The ohmic contacts of this invention retain this ratio approximately constant over a finite voltage range.

Low loss contacts make it possible to have a capacitor in which whatever losses there are, are primarily in the dielectric. A low loss contact adds only a negligible amount of loss to a dielectric-electrode combination. In a capacitor with lossy contacts, the total loss goes up as the dielectric thickness is reduced while maintaining the same field. It is in this sense that the phrase "low loss contact" is employed herein.

Since it is obvious that many changes and modifications can be made in the above-described details without departing from the nature and spirit of the invention, it is to be understood that the invention is not limited to said details except as set forth in the appended claims.

What is claimed is:

1. A method of preparing an ohmic contact for an electrical device comprising: applying to the surface of an inorganic substrate having a strongly electronegative element thereon an intimate mixture throughout of (1) a first metal selected from the platinum group metals and mixtures thereof, and (2) at least one second metal selected from calcium, magnesium, strontium, barium, zinc, tin, vanadium, titanium, indium, nickel and chromium; and subjecting the applied intimate mixture and substrate to a temperature between about 1000-2500° F. for a time sufficient to cause oxidation of at least some of said second metal with at least some of said electronegative element, thereby forming an ohmic or low loss contact to said substrate.

2. The method of claim 1 wherein said intimate mixture throughout is applied having said first metal in powdered form and said second metal in the form of a metalorganic compound of the formula MZ_x , wherein M is said second metal; Z is R, OR, SR or OCOR; R is a C_1 - C_{20} organic group; and x is 2-4.

3. The method of claim 1 wherein said intimate mixture throughout is applied to said substrate by the simultaneous evaporation of said first metal and said second metal under pressure conditions of 10^{-3} torr or less.

4. The method of claim 1 wherein said first metal is present in from 50-99% by weight, and said second metal is present in from 1-50% by weight.

5. The method of claim 2 wherein said inorganic substrate is a ceramic titanate doped to semiconductivity;

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said first metal is powdered palladium; said second metal is zinc octanoate; and said substrate is fired at 2200° F. for a period of ten minutes.

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ALFRED L. LEAVITT, Primary Examiner
M. F. ESPOSITO, Assistant Examiner

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