

Description

This invention relates to a method of forming a thick film resistor circuit on a substrate comprising depositing a paste including a metal component comprising primarily copper on the substrate; heating the structure in an oxidizing atmosphere to bond the metal component to the substrate, forming a resistor material on said substrate and on portions of said metal, heating the resulting structure in an oxidizing atmosphere to establish a desired sheet resistance for the resistor material, and heating the structure in a reducing atmosphere to establish a desired sheet resistance for the metal without significantly affecting the resistor material.

At the present time, most thick film circuits employ a conductor system based on the noble metals silver, gold, palladium and platinum, alone or in combination, and ruthenium-based resistor material. Precious metal pastes, though providing high conductivity, are fairly costly. In addition, silver-based pastes can result in migration of silver across the substrate to cause short circuits. Furthermore, poor solderability often results when noble-metal systems are used.

In view of the above problems, workers in the art have proposed alternatives to the noble-metal system and in particular the use of copper-based conductors. For example, copper pastes which are deposited and fired in a nitrogen atmosphere have been developed (see, e.g., U.S. Patent 4,072,771 issued to Grier). However, such pastes are incompatible with ruthenium-based resistor materials which require firing in an oxidizing atmosphere.

Other proposals have been made which permit a copper paste conductor requiring a reducing atmosphere to be fabricated along with resistors requiring an oxidizing atmosphere. For example, we previously suggested depositing a fritless copper paste, firing at a high temperature, then reducing the material and re-oxidizing to form a low density copper oxide. The resistors were then deposited and fired in air, followed by reducing the copper oxide at a sufficiently low temperature so as not to degrade the resistors (see U.S. Patent 4,140,817, issued to Brown et al). Although effective the process required a high initial firing in a special furnace and extra process steps. Therefore, we later proposed using a fritted copper paste which could be fired at a low temperature. After the resistors were formed, the material could be reduced at a low temperature which did not significantly affect the resistors (see U.S. Patent 4,316,920 issued to Brown et al). While such a process was satisfactory, a need still existed for improved conductivity, adhesion and solderability of the conductor material.

Solid State Technology, May 1972, pp 46-50 and 72 is directed to the formation of copper conductors utilizing a paste which is first fired in an oxidizing atmosphere and then reduced after carrying out all normal circuit processing in the usual way. It is also suggested that a copper silver

eutectic alloy could be made to adhere to a ceramic substrate.

According to the present invention there is provided a method of forming a thick film resistor circuit on a substrate, comprising depositing on the substrate a paste including a metal component comprising copper and silver; heating the structure in an oxidizing atmosphere at a temperature of less than 1100 degrees C to bond the metal component to the substrate, forming a resistor material on said substrate and on portions of said metal, heating the resulting structure in an oxidizing atmosphere to establish a desired sheet resistance for the resistor material, and heating the structure in a reducing atmosphere to establish a desired sheet resistance for the metal without significantly affecting the resistor material, characterized by using a fritless paste including 1-25 percent silver, and up to 10 percent aluminum, by weight of the metal component.

In the drawing, the Figure is a cross-sectional view of a portion of a thick film circuit fabricated in accordance with one embodiment of the invention. It will be appreciated that the Figure is not necessarily drawn to scale.

The Figure illustrates a portion of a thick film circuit. It will be appreciated that a typical circuit includes many conductive and resistive elements along with other components.

The circuit is fabricated on an insulating substrate, 10, which is typically alumina. In order to form the conductive pattern (11, 12), a suitable thick film paste was first prepared.

In accordance with a feature of the invention, the paste, which is fritless, includes a metal component which comprises primarily copper and includes a small amount of silver. The copper and silver could be present as an alloy, as a silver-coated copper particle, or as a mixture, although an alloy is preferred. The Cu/Ag alloy can be formed by sintering at a temperature just below the melting point of the alloy or by jet atomization in the liquid state. It was discovered that the addition of silver to the copper paste enhances the bonding mechanism with the substrate and therefore permits firing at a low temperature after deposition without the need for frits in the paste. The conductivity, adhesion and solderability of a conductor formed from a fritless paste has been found to be generally superior to one formed from a fritted paste when subjected to oxidation and then reduction reactions.

It is recommended that the Cu/Ag combination contain as little silver as possible to keep migration of silver to other portions of the circuit at a low level. The combination should be less than 25 percent silver and preferably less than 10 percent. A minimum percentage of silver is approximately 1 percent.

The metal component of the paste may also include a small amount of aluminium which apparently helps prevent the oxidation of copper during powder processing, acts as a protective coat for the Cu/Ag particles, contributes to the

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formation of the interface with certain alumina surfaces upon firing, and improves the resistance of the fired conductor to the leaching action of molten tin in a subsequent soldering process. A preferred range for the aluminum is apparently 0.1—1.0 percent.

The paste also includes an organic vehicle to permit screen printing. Typically, the vehicle includes a binder and at least one solvent. In this example, the vehicle was ethyl cellulose dissolved in a binary solvent of alpha terpineol and butyl carbitol acetate. The binder preferably comprises 3—20 percent of the vehicle and either of the two solvents can be varied from 0—100 percent of the solvent for the vehicle.

In a particular example, a 10,000 gm batch of the alloy was prepared by taking 9100 gms of copper, 800 gms of silver, and 100 gms of aluminum and alloying the two by jet atomization of the liquid metal using argon gas. Meanwhile, a 10 percent solution of the vehicle was formed by mixing 10 gms of binder and 45 gms of each of the solvents. A portion of the metal powder particles having a size of 25 μ m or less was mixed with the organic vehicle to form a thick film paste. In this example, the paste was approximately 85 percent by weight of the metal and 15 percent by weight of the vehicle (85 gms of powder and 15 gms of vehicle). However, a useful range for the metal is 10—90 percent of the paste depending on particular needs.

The conductor paste was deposited on the substrate, 10, to form the desired conductor pattern (11, 12) by means of standard screen-printing. The thickness of the paste after drying at 125 degrees C for approximately 10 minutes was approximately 0.00254 cm (0.001 in.), although a thickness in the range 0.00127—0.00508 cm (0.0005—0.002 in.) would be useful.

In order to bond the metal component to the substrate, the deposited paste was fired in air. In this example, the peak firing temperature was 1,000 degrees C for 8—10 minutes in a standard belt kiln. Total heating time was 1 hr. where the temperature was first increased at a rate of 60 degrees C per minute and then decreased at a rate of 60 degrees C per minute. One of the significant features of the invention is the fact that the metal is bonded at such a low temperature, which permits reduction at a low temperature later in the processing. The maximum firing temperature useful for such a process appears to be 1100 degrees C. A preferred minimum temperature is approximately 950 degrees C.

As a result of firing, essentially all of the organic vehicle is evaporated, and what is left is a layer comprising mainly copper oxide and a thin glue layer (approximately $0.127 \cdot 10^{-3}$ cm (0.05 mils) thick) between the copper and substrate which consists essentially of copper aluminates and aluminates (CuAl_2O_4 , CuAlO_2), silver aluminates (AgAlO_2), and CuO . The presence of silver or silver oxide could not be detected by x-ray analyses, and so if they are present, it is in an amount of less than 5 percent.

After the desired conductor pattern is formed, a resistor material (13) was then deposited on selected portions of the substrate and conductors. In this particular example, the resistor was formed from a standard paste comprising a bismuth ruthenate and lead boro-silicate glass sold by DuPont under the designation "Birox". However, the invention could be used with any resistor material firable in an oxidizing atmosphere, although it is particularly beneficial with any ruthenium-based resistor material.

The resistor paste was dried by heating the structure at 125 degrees C for 10 minutes, which times and temperatures are not critical. The thickness of the resistor after drying was approximately $2.032 \cdot 10^{-3}$ cm (0.8 mils), and usually ranges from $1.778 \cdot 10^{-3}$ — $2.286 \cdot 10^{-3}$ cm (0.7—0.9 mils).

Next, the desired sheet resistance of the resistors was achieved by firing the structure in air at temperatures and times which will vary according to the particular material and the desired sheet resistance. In this example, the firing was done at a peak temperature of 850 degrees C for 10 minutes to achieve a sheet resistance of approximately 1,000 ohms per square. The total firing cycle was 60 minutes, with the temperature increasing at a rate of 35 deg./min. and then decreasing at rate of 45 deg./min.

Following the oxidation of the resistors, the desired sheet resistance of the conductors (11, 12) was established by heating the structure in a reducing atmosphere. In this particular example, the structure was heated in a belt kiln in an atmosphere of 10 percent H_2 and 90 percent N_2 at a peak temperature of 400 degrees C for 30 minutes. Total heating time was 90 minutes where the temperature rose at a rate of 20 degrees C per minute and decreased at a rate of 20 degrees C per minute. As mentioned previously, an important advantage of the invention is the fact that the initial firing of the paste in air at a low temperature permits the reduction at a sufficiently low temperature so that the resistors are not adversely affected. In general, a useful heating range is 250—400 degrees C peak temperature for 15—60 minutes. The particular sheet resistance achieved here for the conductors was 0.0035 ohms per square, and a sheet resistance of less than 0.005 ohms per square is preferred. Although an H_2/N_2 atmosphere was used, any reducing atmosphere could probably be employed.

It should be understood that in the context of the present application, the term "metal component" is intended to include the oxides of the metals as well as the metals themselves. Further, other organic vehicles can be used as long as they provide the desired rheological properties for application of the paste. The vehicle should be thixotropic, have a viscosity for good screen-printing and be removable during firing at a low temperature and rate to avoid cracks and voids.

Claims

1. A method of forming a thick film resistor circuit on a substrate comprising depositing on the substrate (10) a paste (11, 12) including a metal component comprising copper and silver; heating the structure in an oxidizing atmosphere at a temperature of less than 1100 degrees C to bond the metal component to the substrate, forming a resistor material (13) on said substrate and on portions of said metal, heating the resulting structure in an oxidizing atmosphere to establish a desired sheet resistance for the resistor material, and heating the structure in a reducing atmosphere to establish a desired sheet resistance for the metal without significantly affecting the resistor material, characterized by using a fritless paste including 1—25 percent silver, and up to 10 percent aluminum, by weight of the metal component.

2. The method according to claim 1, characterized by using the paste including aluminum in an amount of 0.1—1.0 percent.

3. The method according to claim 1, characterized by using the paste including silver preferably in an amount of 1—10 percent by weight of the metal component.

4. The method according to claim 1, characterized in that the resistor material being used in forming the circuit comprises ruthenium-based components.

5. The method according to claim 1, characterized by conducting said heating in the reducing atmosphere to establish final sheet resistance for the metal of less than 0.005 ohms per square.

6. The method according to claim 1, characterized by obtaining the desired sheet resistance of the metal by heating at a peak temperature of 250—400 degrees C for 15—60 minutes.

7. The method according to claim 1, characterized in that the substrate comprises alumina.

8. The method according to claim 1, characterized in that the paste further comprises an organic vehicle comprising a binder and at least one solvent.

Patentansprüche

1. Verfahren zum Herstellen einer Dickschichtwiderstands-Schaltung auf einem Substrat, umfassend

—Niederschlagen einer Paste (11, 12), die eine Kupfer und Silber umfassende Metallkomponente enthält, auf dem Substrat (10),

—Erwärmen der Anordnung in oxidierender Atmosphäre bei einer Temperatur kleiner als 1100°C, um die Metallkomponente an das Substrat zu bonden,

—Ausbilden eines Widerstandsmaterials (13) auf dem Substrat und auf Teilen des Metalles,

—Erwärmen der resultierenden Anordnung in oxidierender Atmosphäre zum Erhalt eines gewünschten Flächenwiderstandswertes für das Widerstandsmaterial und

—Erwärmen der Anordnung in reduzierender

Atmosphäre zum Erhalt eines gewünschten Flächenwiderstandswertes für das Metall ohne nennenswerte Beeinträchtigung des Widerstandsmaterials, gekennzeichnet durch

—Verwendung einer frittlosen Paste, die 1—25-Silber und bis zu 10% Aluminium, bezogen auf das Gewicht der Metallkomponente, enthält.

2. Verfahren nach Anspruch 1, gekennzeichnet durch

—Verwendung der Aluminium in einem Anteil von 0,1 bis 1,0% enthaltenden Paste.

3. Verfahren nach Anspruch 1, gekennzeichnet durch

—Verwendung der Silber vorzugsweise in einem Anteil von 1 bis 10 Gew.-% der Metallkomponente enthaltenden Paste.

4. Verfahren nach Anspruch 1, dadurch gekennzeichnet, daß

—das bei der Ausbildung der Schaltung verwendete Widerstandsmaterial Komponenten auf Ruthenium-Basis umfaßt.

5. Verfahren nach Anspruch 1, gekennzeichnet durch

—Ausführen der Erwärmung in der reduzierenden Atmosphäre zum Erhalt eines Schließlichen Flächenwiderstandswertes für das Metall von weniger als 0,005 Ohm/Quadrat.

6. Verfahren nach Anspruch 1, gekennzeichnet durch

—Erhalten des gewünschten Flächenwiderstandswertes des Metalles durch 15 bis 60 Minuten langes Erwärmen auf eine Spitzentemperatur von 250 bis 400°C.

7. Verfahren nach Anspruch 1, dadurch gekennzeichnet, daß

—das Substrat Aluminium oxid umfaßt.

8. Verfahren nach Anspruch 1, dadurch gekennzeichnet, daß

—die Paste des weiteren einen organischen Träger, der ein Bindemittel und wenigstens ein Lösungsmittel enthält, umfaßt.

Revendications

1. Un procédé de formation d'un circuit de résistance à couche épaisse sur un substrat, comprenant le dépôt sur le substrat (10) d'une pâte (11, 12) qui contient un composant métallique comprenant du cuivre et de l'argent; le chauffage de la structure dans une atmosphère oxydante à une température inférieure à 1100°C, pour faire adhérer le composante métallique au substrat, la formation d'une matière résistive (13) sur le substrat et sur des parties du métal, le chauffage de la structure résultante dans une atmosphère oxydante pour établir une résistance carrée désirée pour la matière résistive, et le chauffage de la structure dans une atmosphère réductrice pour établir une résistance carrée désirée pour le métal, sans affecter notablement la matière résistive, caractérisé par l'utilisation d'une pâte sans fritte comprenant 1 à 25% d'argent et jusqu'à 10% d'aluminium, en poids du composante métallique.

2. Le procédé selon la revendication 1, caracté-



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rise par l'utilisation d'une pâte contenant de l'aluminium dans une proportion de 0,1 à 1.0%.

3. Le procédé selon la revendication 1, caractérise par l'utilisation d'une pâte contenant de l'argent, de préférence dans une proportion de 1 à 10% en poids du composant métallique.

4. Le procédé selon la revendication 1, caractérise en ce que la matière résistive qui est utilisée pour former le circuit comprend des composants à base de ruthénium.

5. Le procédé selon la revendication 1, caractérise par l'accomplissement du chauffage dans l'atmosphère réductrice pour établir une résis-

tance carrée finale pour le métal inférieure à 0,005 ohm par carré.

6. Le procédé selon la revendication 1, caractérise par l'obtention de la résistance carrée désirée pour le métal par chauffage à une température maximale de 240—400°C pendant 15—60 minutes.

7. Le procédé selon la revendication 1, caractérise en ce que le substrat consiste en alumine.

8. Le procédé selon la revendication 1, caractérise en ce que la pâte comprend en outre un véhicule organique qui comprend un liant et au moins un solvant.

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