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**ELECTRODEPOSITION OF LOW TEMPERATURE, HIGH
CONDUCTIVITY, POWDER MATERIALS FOR ELECTRICALLY
CONDUCTIVE PASTE FORMULATIONS**

FIELD OF THE INVENTION

The present invention relates to novel interconnection materials for forming electroconductive connections between electroconductive members, and to the method for producing such electroconductive connections. In addition, this invention addresses environmentally-safe materials and processes, which can be an alternative to lead (Pb)-containing solder connection technology.

BACKGROUND

Most electrical conductors used in electronic devices are made of metals, such as copper, aluminum, gold, silver, lead/tin (solder), molybdenum and others. Solder connection technology using lead/tin alloys plays a key role in various levels of electronic packaging, such as flip-chip connection (or C4), solder-ball connection in ball-grid-arrays (BGA), IC package assembly to a printed circuit board (PCB). Solder joints produced in the electronic packages serve critically as electrical interconnections as well as mechanical/physical connections. When either of the functions is out of service, the solder joint is considered to have failed, which can often threaten a shut-down of the whole electronic system.

When microelectronic packages are assembled to a printed circuit board, the lead-tin eutectic solder, 63%Sn-37%Pb, having the lowest melting point (183 °C) among Pb-Sn alloys, is most widely used. In these applications, there are two solder connection technologies employed for mass production: plated-through-hole (PTH) and surface mount technology (SMT) soldering. The basic difference between the two technologies originates from the difference in the PCB design and its interconnection scheme.

In SMT soldering, microelectronic packages are directly attached to the surface of a PCB. A major advantage of SMT is high packaging density, which is realized by eliminating most PTH's in the PCB as well as by utilizing both surfaces of the PCB to accommodate components. In addition, SMT packages have a finer lead pitch and a smaller package size compared to traditional PTH packages. Hence, SMT has contributed significantly in reducing the size of electronic packages and thereby the volume of the overall system.

In SMT soldering, solder paste is applied to a PCB by screen printing. Solder paste consists of fine solder powder, flux, and organic vehicles. During the reflow process, solder particles are melted, flux is activated, solvent materials are evaporated, and simultaneously molten solder coalesces and is eventually solidified. In contrast, in the wave soldering process, a PCB is first fluxed and components are mounted on it. Then it is moved over a wave of molten solder.

The soldering process is usually completed by subjecting the solder joints to a cleaning step to remove residual flux materials. Due to environmental concerns, CFCs and other harmful cleaning agents are being eliminated and replaced by either water-soluble or no-clean flux materials.

Recent advances in microelectronic devices demand a very fine pitch connection between electronic packages and a printed circuit board (in an order of a few hundred micrometer pitch). The current solder paste technology used in SMT can not handle this very fine pitch interconnection due to the soldering defects such as bridging or solder balling. Another technical limitation of using the Pb-Sn eutectic solder is its high reflow temperature, approximately 215 °C. This temperature is already higher than the glass transition temperature of the epoxy resin used in most polymeric printed circuit board materials. Thermal exposure at this reflow temperature produces significant thermal strains in a printed circuit board after soldering, especially in the direction perpendicular to the surface of a PCB, where no structural reinforcement is made in that direction. Thereby, the residual thermal strains in an assembled PCB would cost the reliability of an electronic system.

A more serious concern regarding the usage of lead (Pb)-containing solders is an environmental issue, which we have experienced the trend/impact already in other industries by eliminating lead from gasoline and paints.

In the electronic industry, two different groups of materials are investigated currently for the possibility of substituting the Pb-containing solder materials; Pb-free solder alloys, and electrically conductive pastes (ECP). The present invention discusses the development and applications of the electrically conductive paste materials. An electrically conductive paste (or adhesive) is made of metallic filler particles loaded in the matrix of a polymer material. Silver-particle filled epoxy is the most common example of the electrically conductive pastes 6, schematically shown in FIG. 1. The silver particles 2 usually in a shape of flakes provide electrical conduction by percolation mechanism, while the epoxy matrix 4 provides adhesive bond between a component 8

and a substrate 10. This silver-filled epoxy material has been long used in the electronic applications as a die-bonding material, where thermal conduction rather than electrical conduction property is utilized. However, this material has not been accepted for the applications requiring high electroconduction and fine pitch connection. The silver-filled epoxy material has several limitations, such as low electrical conductivity, increase in contact resistance during thermal exposure, low joint strength, silver migration, difficulty in rework, and others. Since this silver-filled epoxy material is electrically conductive in all the directions, it is classified as "isotropic" in electro-conduction. There is another class of electrically conductive adhesive (or film), which provides electroconduction only in one direction. This class of the materials is called as "anisotropic" conductive adhesive 12 or film, shown schematically in FIG. 2. The anisotropic conductive adhesive 12 or film becomes conductive only when it is compressed between two conducting pads 22 and 24. This process requires normally heat and pressure. The major application of the anisotropic conductive film is for joining of a liquid crystal display panel to its electronic printed circuit board. The conducting particles 14 are usually deformable, such as solder balls, or plastic balls coated with nickel and gold. The binder or adhesive material 16 is mostly a thermosetting resin.

In our recent invention (641,406), an electrically conductive paste (ECP) material is disclosed, which consists of copper powder coated with a thin layer of low melting point, Pb-free metals, such as Sn, In, Bi, Sb and their alloys, mixed with an environmentally-safe fluxing agent, and dispersed in the matrix of thermoplastic or thermosetting polymers. The microstructure of the ECP containing Sn-coated 64 Cu powder 62 is shown in its cross-section view in FIG. 3.

The ECP made of Sn-plated Cu powder and polyimide-siloxane resin is a good candidate for the high temperature solder joints such as C4 and solder ball connection (SBC) to a ceramic substrate. However, for the polymeric printed circuit board applications, this ECP is not adequate, because the reflow temperature such as 250 °C is much higher than the glass transition temperature of the polymeric resin, for example, FR-4. A candidate for this purpose is an ECP made of Indium-plated Cu powder formulated with polyimide-siloxane resin. The reflow temperature of the Indium-plated Cu powder paste is expected to be about 180 °C, which is even lower than the reflow temperature of the Pb/Sn eutectic solder, 215 °C.

In our recent invention (414070 , 414063), we disclosed structure and methods of fabricating dendritic powder materials for high conductivity paste applications as shown in Fig. 4. The copper dendrite structure 44 was deposited on a dummy substrate 40, followed by another electrodeposition of a low melting point metal 42 (In, Sn, Zn, Bi, and Sb and their alloys) on top of the copper dendrite structure. The dendrite powder was then collected from the substrate and mixed with either thermoplastic or thermoset polymer resin(s) to form an electrically conductive paste.

In the prior art, a solder/polymer composite paste material is disclosed in U. S. Pat. No.5,062,896 (Huang et. al.), comprising a major proportion of a meltable solder powder filler, such as Bi-Sn, Pb-Sn, Bi-Sn-Pb alloys, a minor proportion of a thermoplastic polymer such as a polyimide siloxane, and a minor proportion of a fluxing agent. An oxide-free, partially coalesced solder alloy connection is obtained, which is polymer strengthened and reworkable at a low reflow temperature, per se, or in the presence of polymer solvent.

In a similar prior art, U. S. Pat. No.5,286,417 (Mahmoud et. al.), a fusible conductive adhesive is disclosed, which comprises metal alloy fillers such as Sn-Au and Bi-Au, and a thermoplastic polymer having a glass transition temperature overlapping the melting temperature of the metal filler alloys. The loading of the conductive material in the polymer is in the range of about 15% to about 20% by weight.

In another prior art, U. S. Pat. No.5,136,365 (Pennisi et. al.), an adhesive material is disclosed, which contains a fluxing agent and metal particles for use in reflow soldering such as Sn, Pb, In, Bi, Sb, Ag and others, in the matrix of an epoxy resin. Upon reflow soldering, the said adhesive forms anisotropic electroconduction between an electrical component and a substrate.

In another prior art, U. S. Pat. No.5,213,715 (Patterson et. al.), a directionally conductive polymer is disclosed, which contains a metallic filler powder of Ni or Cu. The metallic powder is treated by a different polymer than the polymer used as a matrix resin. Upon compression, the coated polymer is displaced to make an electrical conduction among the filler particles.

SUMMARY

It is an object of the present invention to provide an electrically conductive paste material which is environmentally safe and low cost.

It is an object of the present invention to provide an electrically conductive paste material which produces a higher electrical conductivity than the conventional silver-filled epoxy does.

It is an object of the present invention to provide an electrically conductive paste material which can be processed at a lower temperature than the reflow temperature of Pb-Sn eutectic solder paste.

It is an object of the present invention to provide an electrically conductive paste material which is more corrosion-resistant than the conventional silver-filled epoxy pastes.

In one particular embodiment, we disclose an electrodeposited powder structure consisting of Sn(undercoat)/Cu(dendrite)/Sn(barrier)/In (overcoat). This powder structure is sequentially electrodeposited on a dummy substrate such as titanium or stainless steels, from which the electrodeposited material can easily be separated. The undercoat Sn layer provides protection of Cu surface from oxidation or corrosion as well as controls the composition of the overcoat layer when they are in contact to form metallurgical bonding among the powder particles. The Sn barrier layer slows down the fast Cu-In compound formation, which can prevent the particle-to-particle bonding. The In overcoat together with the Sn undercoat and the barrier enables to make the particle-to-particle bonding at a low temperature such as 150 °C. The thickness of undercoat, barrier and overcoat layers is approximately in the range of 1 micro-meter or less. The Cu dendrite size is in the range of 1 to 50 micro-meter in length.

In another particular embodiment, we disclose an electrodeposited powder structure consisting of Sn(undercoat)/Cu(dendrite)/Bi-Sn alloy(overcoat). In this structure no barrier layer between Cu and Bi-Sn metals was required. The Bi-Sn overcoat layer was electrodeposited as the near-eutectic composition by using a commercial plating solution.

The as-collected electrodeposited powder particles have a wide variation in the particle size. In order to obtain a uniform particle size, either a jet milling process or ultrasonic particle size reduction method was required in conjunction with a micro-sieve screening process. The preferred particle size distribution is in the range of 5 to 10 micro-meter.

The electrodeposited powder with a uniform and preferred particle size is then mixed with either thermoplastic or thermoset polymer resin(s) to formulate an electrically conductive paste as described in our previous inventions (414070 , 414063).

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a schematic illustration of an electrically conductive paste comprising silver flake particles as a filler in the matrix of epoxy resin. The conductive paste is classified as isotropic in electroconduction. (prior art)

FIG. 2 is a schematic illustration of an electrically conductive adhesive which becomes electrically conductive only in the one direction when the adhesive film is compressed between two contact or bond pads. The conductive adhesive (or film) is classified as anisotropic. (prior art)

FIG. 3 is a schematic illustration of an electrically conductive paste material, comprising spherical copper powder filled in the matrix of thermoplastic polymer resin. The copper particles are coated with a low melting point, non-toxic metals, such as tin, indium, bismuth, and others.

FIG. 4 is a schematic illustration of the dendritic copper powder deposited on a dummy substrate, followed by electrolytic deposition of a thin layer of indium metal on the dendritic powder.

FIG. 5 is a schematic illustration of a new electrodeposited powder structure deposited on a dummy substrate; Sn(undercoat)/Cu(dendrite)/Sn(barrier)/In(overcoat).

FIG. 6 is a schematic illustration of a new electrodeposited powder structure deposited on a dummy substrate; Sn(undercoat)/Cu(dendrite)/Bi-Sn(overcoat).

DETAILED DESCRIPTION

In the previous inventions, 414,070 and 414,063, we disclosed the copper dendrite structure deposited on a dummy substrate, followed by an electrodeposition of thin indium metal on top of the copper dendrite structure. The indium-coated copper dendrite powder can be easily collected by scraping from the dummy substrate. The detailed conditions for the copper dendrite electrodeposition were disclosed as the three-stage plating scheme; (i) initial plating of dense copper, (ii) dendrite nucleation stage, and (iii) dendrite growth stage.

The indium plating condition and bath were also disclosed.

Fig. 5 is a schematic illustration of a new electrodeposited powder structure deposited on a dummy substrate 50;

Sn(undercoat)52/Cu(dendrite)54/Sn(barrier)56/In(overcoat)58. The undercoat Sn 52 and barrier Sn layer 56 were electrodeposited by using the Solderon Tin Concentrate

solution from LeaRonol, Inc. The Sn barrier layer can be replaced by other metals and alloys, such as Ni, Co, Cr, Fe, Pd and their alloys.

Fig. 6 is a schematic illustration of a new electrodeposited powder structure deposited on a dummy substrate 60; Sn(undercoat)62/Cu(dendrite)64/Bi-Sn(overcoat)66. The overcoat Bi-Sn layer 66 is deposited as a Bi-Sn alloy whose composition is near eutectic, 60%Bi-40%Sn in weight. The Bi-Sn alloy layer was deposited by using an experimental bath consisting of Solderon Tin Concentrate, Solderon Bi Concentrate, Solderon Acid, Solderon Bi Primary and Solderon Bi Secondary solutions from LeaRonol, Inc. Typical electrodeposition conditions for the Sn/Cu/Bi-Sn powder materials are as follows;

- i) Sn (undecoat); 2 A, 0.5 V, 3 min, for 100 in² area,
- ii) Cu (dendrite); 20 A, 2.5 V, 2 min, for 100 in² area,
- iii) Bi-Sn (overcoat); 14 A, 2.0 V, 2 min, for 100 in² area.

The anode material for Cu plating was an oxygen-free copper metal, and for Sn and Bi-Sn plating was a pure tin metal.

The as-collected electrodeposited powder particles have a wide variation in the particle size. In order to obtain a uniform particle size, either a jet milling process or ultrasonic method was required in conjunction with a micro-sieve screening process. The preferred particle size distribution is in the range of 5 to 10 micro-meter.

The electrodeposited powder of a uniform and optimum particle size range is stored in the "no-clean" flux, Qualitek #305, until it is used for paste formulation. Electrically conductive paste is formulated by dispersing the filler powder of uniform and desired

particle size in the matrix of either thermoplastic or thermoset polymeric resin as described in the previous inventions (414070, 414063).

In order to characterize the electrical and mechanical properties, the joint samples with the low temperature, Pb-free conductive paste were made by joining two "L-shaped" copper coupons. A joining operation was performed at 180 °C, 15 min, 25 psi. The model joints made of the Sn/Cu/Bi-Sn with a polyimide siloxane resin showed excellent electrical and mechanical properties compared to those of the solder joints.



CLAIMS

What is claimed is:

1. A structure comprising:

a plurality of dendrites of a material;

said dendrites having a central portion and branched filaments projecting away from said central portion; and

said dendrites have a first coating on a first portion of said dendrites and a second coating on a second portion of said dendrites.

2. A structure according to claim 1, wherein said plurality of dendrites is a powder.
3. A structure according to claim 1, wherein said material is selected from the group consisting of Cu, Pd, Pt, Ni, Ag and Au.
4. A structure according to claim 1, wherein said first coating is a material selected from the group consisting of In, Sn, Zn, Pb, Bi and Sb and a second coating is a different material selected from the group consisting of In, Sn, Zn, Pb, Bi and Sb.
5. A structure according to claim 3, wherein at least some of said dendrites are fused to others of said dendrites through said electrically conductive coating.

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6. A structure according to claim 1, wherein said plurality of dendrites are embedded within a polymeric material.
7. A structure according to claim 1, wherein said structure is an electrical interconnection means.
8. A structure according to claim 1, wherein said electrically conductive coating has a melting temperature less than that of said dendrites.
9. A structure according to claim 1, further including a first and a second surface between which said structure is disposed to provide interconnection between said first and second surfaces.
10. A structure according to claim 6, wherein said polymeric material is cured or baked.
11. A structure according to claim 6, wherein said polymeric material is selected from the group consisting of polyimide, siloxane, polyimide siloxane, epoxy, and bio-based polymeric resins derived from lignin, cellulose, wood oil and crop oil.
12. A structure according to claim 6, wherein said polymeric material is a solvent-containing thermoplastic adhesive.
13. A structure according to claim 6, wherein said polymeric material is a solvent-free thermoplastic adhesive.





14. A structure according to claim 9, wherein said plurality of dendrites are embedded within a polymeric material which provides adhesive joining of said first and said second surfaces.
15. A structure according to claim 9, wherein said first surface is a first electronic device contact location and wherein said second surface is a second electronic device contact location.
16. A structure according to claim 15, wherein said first electronic device is a semiconductor chip and said second electronic device is a packaging substrate.
17. A structure according to claim 9, wherein one of said first and said second surfaces is a solder surface.
18. A structure according to claim 9, wherein said structure is an electronic device.
19. A structure according to claim 9, wherein said structure is a computing device.
20. A structure comprising:

a network of interconnected dendrites having spaces therebetween;

each of said dendrites having a first coating and a second coating on a second portion of said dendrites thereon of a fusible material;

adjacent dendrites in said network adhered together through said fusible material.

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21. A structure according to claim 20, wherein said spaces contain a polymeric material.
22. A structure according to claim 20, wherein said dendrites have a central portion and branched filaments projecting away from said central portions.
23. A structure according to claim 1, wherein said dendrites have a length and a width and an aspect ratio which is a ratio of said length to said width.
24. A structure according to claim 23, wherein said aspect ratio is between about 1 to about 10.
25. A structure according to claim 23, wherein said aspect ratio is between about 1 to about 5.
26. A structure according to claim 20, wherein said material is electrically conductive.
27. A structure according to claim 6, wherein said dendrites are from about 10% to about 90% by weight of said structure.
28. A structure according to claim 6, wherein said polymeric material is selected from the group consisting of a polyimide, a siloxane, a polyimide-siloxane, an epoxy, and a bio-based polymer resin.
29. A structure according to claim 9, wherein said coating forms a metallurgical bond to said first and said second surfaces.

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30. A structure according to claim 9, wherein said first and said second surfaces are electrically conducting.
31. A structure according to claim 1, wherein said coating is electrically conductive.
32. A structure according to claim 6, further including a solvent, butyric acid and ethylene glycol.
33. A structure according to claim 6, further including a solvent, and a 'no-clean' flux containing a low residue, halogen-free activator.
34. A structure according to claim 6, wherein said polymeric material is a solvent-free thermoset adhesive.
35. A structure according to claim 6, wherein said polymeric material is a soluble epoxy.
36. A structure according to claim 35, wherein said soluble epoxy is selected from the group consisting of a ketal and a acetal diepoxide.
37. A structure comprising:

a plurality of copper dendrites;

said dendrites having a central Cu portion and branched filaments projecting away from said central portion; and

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said dendrites have a first coating on a first portion of said dendrites and a second coating on a second portion of said dendrites, said first coating is Sn and said second coating has a first layer of tin on said copper dendrite and a top layer of In on said Sn layer.

38. A method comprising the steps of:

disposing a platable surface in contact with a first plating solution;

growing dendrites on said surface from said plating solution; and

forming on a first portion of said dendrites a first coating and forming on a second portion of said dendrites a second coating to form coated dendrites.

39. A method according to claim 38, wherein said first plating solution is an electroplating solution.

40. A method according to claim 38, wherein said second plating solution is selected from the group consisting of an electroless plating solution and an immersion plating solution and an electroplating solution.

41. A method according to claim 38, wherein said platable surface is electrically conductive.

42. A method according to claim 38, further including removal of said dendrites with said electrically conductive coating thereon from said surface.





43. A method according to claim 38, wherein said dendrites have a central portion and branched portions extending away from said central portion.
44. A method according to claim 42, wherein said step of removing comprises shaving said dendrites from said surface.
45. A method according to claim 38, wherein said dendrites are formed from an electrically conductive material.
46. A method according to claim 45, wherein said electrically conductive material is selected from the group consisting of Cu, Pd, Pt, Ni, Ag, and Au.
47. A method according to claim 38, wherein said coating is electrically conductive and is formed by immersing said dendrites in a second plating solution.
48. A method according to claim 47, wherein said second plating solution is an electroplating solution.
49. A method according to claim 47, wherein said second plating solution is selected from the group consisting of an electroless plating solution and an immersion plating solution.
50. A method according to claim 38, wherein when said surface is exposed to said first plating solution; a first voltage is applied to said surface to plate said dendrites on said surface; and when said dendrites are exposed to said second





plating solution a second voltage is applied to said dendrites to plate said coating on said dendrites.

51. A method according to claim 38, wherein said first coating is selected from the group consisting of Sn, Zn, In, Bi, Pb, Au, and Sb and wherein said second coating is a different material selected from the group consisting of Sn, Zn, In, Bi, Pb, Au and Sb.
52. A method according to claim 42, wherein a powder is formed from said coated dendrites.
53. A method according to claim 52 further including adding said coated dendrites to a polymeric material to form a paste.
54. A method according to claim 53 further including a solvent, butyric acid, ethylene glycol, and 'no-clean' flux to form a paste.
55. A method according to claim 53, wherein said polymeric material is selected from the group consisting of polyimides, siloxanes, polyimide-siloxanes, epoxies, bio-based resins made from lignin, cellulose, wood oils and crop oils.
56. A method according to claim 53, wherein said paste is disposed between a first and second electrically conductive surface.

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57. A method according to claim 56, wherein said first electrically conductive surface is a chip contact location and said second electrically conductive surface is a substrate contact location.
58. A method according to claim 56, wherein said first electrically conducting surface is a liquid crystal display panel contact location and said second electrically conductive surface is a chip carrier tape lead location.
59. A method according to claim 56, wherein said paste is heated to a first temperature to fuse said coating on adjacent dendrites.
60. A method according to claim 56, wherein said paste is heated to a second temperature sufficient to cure said polymer.
61. A method comprising the steps of:
- growing dendrites on a surface;
- coating said dendrites with a first coating on a first portion of said dendrite and with a second coating on a second portion of said dendrites to form coated dendrites;
- removing said coated dendrites from said surface.
62. A method according to claim 61, wherein said first coating and said second coating are electrically conductive.

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63. A method according to claim 53, wherein said polymeric material is a soluble epoxy.
64. A method according to claim 63, wherein said soluble epoxy is selected from the group consisting of a ketal and a acetal diepoxide.
65. A method according to claim 64, wherein said coated dendrites are dispersed between a first and a second electrically conductive surface.
66. A method according to claim 38, wherein said first coating and said second coating are electrically conductive.
67. A method according to claim 61, further including a solvent, butyric acid and ethylene glycol.
68. A method according to claim 61, further including a solvent, and a 'non-clean' flux containing a low residue, halogen-free activator.
69. A method according to claim 61, further including a polymeric material is a solvent-free thermoset adhesive.
70. A method according to claim 69, wherein said polymeric material is a soluble epoxy.
71. A method according to claim 70, wherein said soluble epoxy is selected from the group consisting of a ketal and a acetal diepoxide.





72. A method comprising the steps of:

disposing a platable surface in contact with a first plating solution;

said surface is Sn on a substrate;

growing Cu dendrites on said platable surface from said plating solution; and

forming on said dendrites a coating to form coated dendrites;

forming on exposed surfaces of said Cu dendrites an Sn layer and on said Sn layer an In layer;

removing said dendrites from said substrate forming a dendritic Cu particle having a first portion coated with Sn and a second portion coated with a layer of In over Sn.

73. A method comprising the steps of:

disposing a platable surface in contact with a first plating solution;

said surface is Sn on a substrate;

growing Cu dendrites on said platable surface from said plating solution; and

forming on said dendrites a coating to form coated dendrites;





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forming on exposed surfaces of said Cu dendrites a Sn-Bi alloy layer;

removing said dendrites from said substrate forming a dendritic Cu particle having a first portion coated with Sn and a second portion coated with a layer of a Sn-Bi alloy.

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