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(54) **CONDUCTIVE INK**

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(57) **ABSTRACT**

A conductive ink is provided. The conductive ink includes a precursor, a reducing agent, and a protective agent, and the precursor includes copper isostearate ($Cu(C_{18}H_{36}O_2)_2$), wherein based on the total weight of the conductive ink, the content of the precursor is 40 wt % to 75 wt %, the content of the reducing agent is 20 wt % to 32 wt %, and the content of the protective agent is 5 wt % to 40 wt %.

CONDUCTIVE INK

CROSS-REFERENCE TO RELATED APPLICATION

[0001] This application claims the priority benefit of Taiwan application serial no. 106133601, filed on Sep. 29, 2017. The entirety of the above-mentioned patent application is hereby incorporated by reference herein and made a part of this specification.

BACKGROUND OF THE INVENTION

Field of the Invention

[0002] The invention relates to a conductive ink, and more particularly, to a copper-containing conductive ink.

Description of Related Art

[0003] To simplify the numerous and complex steps of preparing a conductive circuit via a lithography process, directly printing a conductive ink on a substrate to form a conductive circuit has become a feasible method. In general, the conductive ink with metal as the main component is divided into two types: metal nanoparticle type and organic metal type. In a known conductive ink technique, the resulting conductive layer has a certain thickness, and it is difficult to form a conductive layer having a smaller thickness (such as 1 μm or less). Therefore, the current development trend of a compact and lightweight product is not met.

[0004] Based on the above, the development of a conductive ink with metal as the main component that can form a conductive layer having a smaller thickness (such as 1 μm or less) is an important topic requiring research.

SUMMARY OF THE INVENTION

[0005] The invention provides a conductive ink containing nano copper powders that can form a conductive layer having a smaller thickness (such as 1 μm or less).

[0006] The conductive ink of the invention includes a precursor, a reducing agent, and a protective agent, and the precursor includes copper isostearate ($Cu(C_{18}H_{36}O_2)_2$), wherein based on the total weight of the conductive ink, the content of the precursor is 40 wt % to 75 wt %, the content of the reducing agent is 20 wt % to 32 wt %, and the content of the protective agent is 5 wt % to 40 wt %.

[0007] In an embodiment of the invention, the conductive ink further includes a solvent.

[0008] In an embodiment of the invention, the solvent includes water, toluene, cyclohexane, n-heptane, isooctane, methanol (MeOH), ethanol (EtOH), ethylene glycol (EG), diethylene glycol, or supercritical carbon dioxide.

[0009] In an embodiment of the invention, the reducing agent includes Vitamin C, sodium borohydride ($NaBH_4$), hydrazine (N_2H_4), hydrogen peroxide (H_2O_2), hydrogen (H_2), sodium hypophosphite (NaH_2PO_2), sodium citrate ($Na_3C_6H_5O_7$), potassium sodium tartrate ($NaKC_4H_4O_6$), an amine compound, or an aldehyde compound.

[0010] In an embodiment of the invention, the amine compound includes dimethylformamide (DMF).

[0011] In an embodiment of the invention, the aldehyde compound includes glucose.

[0012] In an embodiment of the invention, the protective agent includes polyacrylic acid (PAA), polyvinyl alcohol (PVA), polyvinylpyrrolidone (PVP), gelatin, sodium dodecyl sulfate (SDS), polyethylene glycol octylphenyl ether (TX-100), cetyltrimethylammonium bromide (CTAB), sodium dioctyl sulfosuccinate (AOT), bis(2-ethylhexyl) phosphoric acid (HDEHP), oleic acid, or dodecaneamine.

[0013] In an embodiment of the invention, the precursor is formed by the reduction reaction of isostearic acid ($C_{18}H_{36}O_2$) and a copper-containing compound.

[0014] In an embodiment of the invention, the copper-containing compound includes $CuSO_4$, $CuCl_2$, $Cu(AOT)_2$, $Cu(NO_3)_2$, $Cu(OH)_2$, or $Cu(acac)_2$.

[0015] Based on the above, the conductive ink of the invention is a nano copper ink with copper isostearate as the precursor and containing a reducing agent and a protective agent, wherein the copper isostearate is formed by the reduction reaction of isostearic acid and a copper-containing compound. A conductive layer having a smaller thickness (such as 1 μm or less) can be formed by the conductive ink of the invention.

[0016] In order to make the aforementioned features and advantages of the invention more comprehensible, embodiments are described in detail below.

DESCRIPTION OF THE EMBODIMENTS

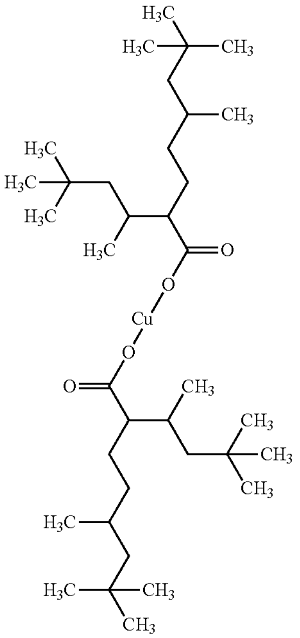
[0017] In the present specification, a range represented by "a numerical value to another numerical value" is a schematic representation for avoiding listing all of the numerical values in the range in the specification. Therefore, the recitation of a specific numerical range covers any numerical value in the numerical range and a smaller numerical range defined by any numerical value in the numerical range, as is the case with the any numerical value and the smaller numerical range stated explicitly in the specification.

[0018] In the following, the embodiments of the invention are described in detail. However, these embodiments are exemplary, and the invention is not limited thereto.

[0019] The invention provides a conductive ink including a precursor, a reducing agent, a protective agent, and a solvent. Hereinafter, the various components above are described in detail.

<Precursor>

[0020] In the present embodiment, the precursor is, for instance, copper isostearate ($Cu(C_{18}H_{36}O_2)_2$) and can be represented by the following chemical structure formula:



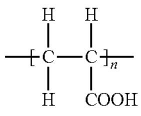
[0021] The copper isostearate is, for instance, formed by the reduction reaction of isostearic acid ($C_{18}H_{36}O_2$) and a copper-containing compound, wherein the copper-containing compound can include $CuSO_4$, $CuCl_2$, $Cu(AOT)_2$, $Cu(NO_3)_2$, $Cu(OH)_2$, or $Cu(acac)_2$, but the invention is not limited thereto. More specifically, the copper isostearate is, for instance, formed by reacting isostearic acid and a copper-containing compound in n-heptane and then removing water and n-heptane via rotary concentration after the reaction. Based on the total weight of the conductive ink, the content of the precursor is, for instance, 40 wt % to 75 wt %.

<Reducing Agent>

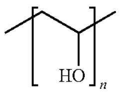
[0022] In the present embodiment, the reducing agent can include Vitamin C, sodium borohydride ($NaBH_4$), hydrazine (N_2H_4), hydrogen peroxide (H_2O_2), hydrogen (H_2), sodium hypophosphite (NaH_2PO_2), sodium citrate ($Na_3C_6H_5O_7$), potassium sodium tartrate ($NaKC_4H_4O_6$), an amine compound, or an aldehyde compound, wherein the amine compound can include dimethylformamide (DMF), and the aldehyde compound can include glucose, but the invention is not limited thereto. Based on the total weight of the conductive ink, the content of the reducing agent is, for instance, 20 wt % to 32 wt %.

<Protective Agent>

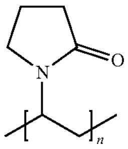
[0023] In the present embodiment, the protective agent can include polyacrylic acid (PAA), polyvinyl alcohol (PVA), polyvinylpyrrolidone (PVP), gelatin, sodium dodecyl sulfate (SDS), polyethylene glycol octylphenyl ether (TX-100), cetyltrimethylammonium bromide (CTAB), sodium dioctyl sulfosuccinate (AOT), bis(2-ethylhexyl) phosphoric acid (HDEHP), oleic acid, or dodecaneamine. The chemical structure formula of each protective agent example above is shown below:



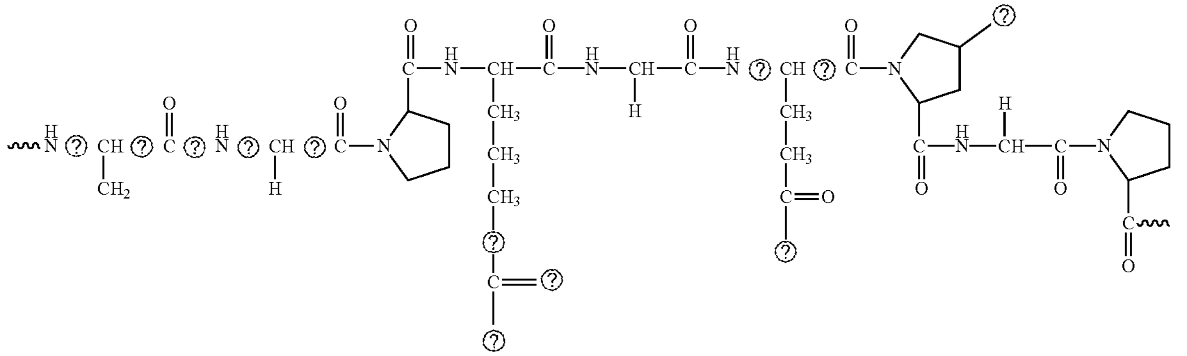
PAA



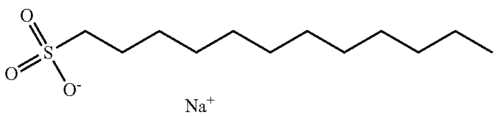
PVA



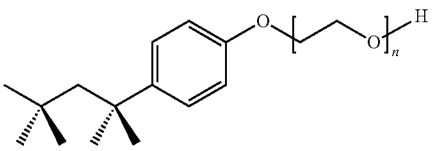
PVP



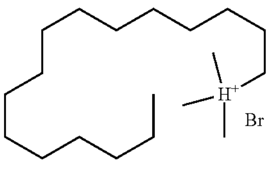
Gelatin



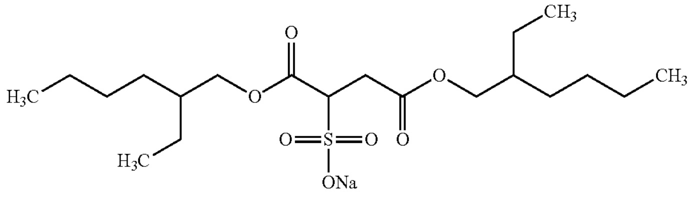
SDS



TX-100

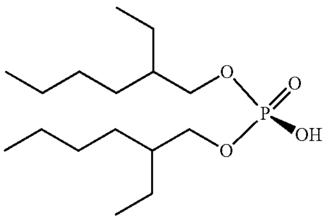


CTAB

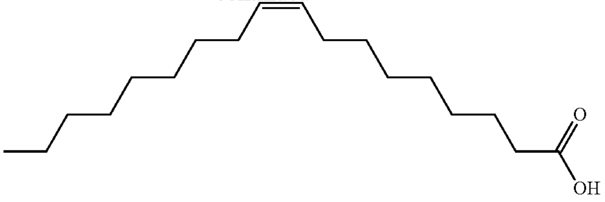


AOT

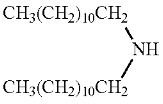
-continued



HDEHP



Oleic acid



Dodecylamine

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[0024] Based on the total weight of the conductive ink, the content of the protective agent is, for instance, 5 wt % to 40 wt %.

<Solvent>

[0025] In the present embodiment, the solvent can include water, toluene, cyclohexane, n-heptane, isooctane, methanol (MeOH), ethanol (EtOH), ethylene glycol (EG), diethylene glycol, supercritical carbon dioxide, or anhydrous alcohol. The solvent is mainly used to dissolve the aforementioned precursor, reducing agent, and protective agent. For instance, in the manufacturing process of the conductive ink of the invention, copper isostearate and polyvinylpyrrolidone (PVP) can be dissolved in anhydrous alcohol, and Vitamin C can be dissolved in methanol and ethylene glycol.

[0026] The conductive ink of the invention can be coated on a substrate, and the solvent, reducing agent, and protective agent can be removed by a heat treatment (heating and sintering) to form a very thin conductive layer (a thickness of, for instance, 1 μm or less). A suitable substrate material is, for instance, polyimide (PI) or glass, but the invention is not limited thereto, and the conductive ink of the invention can also be coated on other substrates on which a conductive layer can be formed.

[0027] In the following, the conductive ink of the embodiments is described in detail via an experimental example. However, the following experimental example is not intended to limit the invention.

Experimental Example

[0028] To prove that the conductive ink provided in the invention can form a very thin conductive layer, the following experimental example is provided.

[0029] The conductive ink of the invention can mainly contain a precursor, a reducing agent, a protective agent, and a solvent. Based on the total weight of the conductive ink, the content of the precursor is 40 wt % to 75 wt %, the content of the reducing agent is 20 wt % to 32 wt %, and the content of the protective agent is 5 wt % to 40 wt %, for example. That is, in the preparation process of the conductive ink of the invention, if 1 g of the precursor is added, then 0.28 g to 0.5 g of the reducing agent and 0.1 g to 1.0 g of the protective agent can be added.

[0030] First, isostearic acid and copper hydroxide were reacted in n-heptane, and then water and the n-heptane were removed after the reaction via rotary concentration to form copper isostearate. Next, copper isostearate and PVP were dissolved in anhydrous alcohol, and Vitamin C was dissolved in methanol and ethylene glycol, and then the components were mixed to form a nano copper suspension solution. The synthesis process of nano copper can be performed in two ways, the first is synthesizing nano copper at room temperature and normal pressure, and the second is synthesizing nano copper in a carbon dioxide expansion liquid. The reaction conditions of the two synthesis methods and each parameter of the resulting nano copper are shown in Table 1 and Table 2 below: Table 1 shows nano copper synthesized under the reaction condition of room temperature, with an average particle size of 200 nm to 300 nm; and Table 2 shows nano copper synthesized in a carbon dioxide expansion liquid, with an average particle size of 150 run to 260 nm.

TABLE 1

Precursor	Solvent			Reducing			Copper	Standard	
Copper isostearate (g)	Anhydrous alcohol (mL)	Methanol (mL)	Ethylene glycol (mL)	agent Vitamin C (g)	Protective agent PVP (g)	Reaction temperature (° C.)	average particle size (nm)	deviation of copper particle size	Conversion rate (%)
1	10	10	10	0.5	0	30	Significant agglutination	Significant agglutination	94.49
					0.1		264	98	86.58
					0.2		255	124	89.25
					0.3		232	103	84.14
					0.4		209	69	84.65
					0.45		207	63	81.51
					0.5		205	56	81.54
					0.55		209	63	78.06
					0.6		233	73	82.51
					0.7		221	71	86.29
					0.8		242	88	83.81

TABLE 1-continued

Precursor	Solvent			Reducing			Copper	Standard	
Copper isostearate (g)	Anhydrous alcohol (mL)	Methanol (mL)	Ethylene glycol (mL)	agent Vitamin C (g)	Protective agent PVP (g)	Reaction temperature (° C.)	average particle size (nm)	deviation of copper particle size	Conversion rate (%)
					0.9		238	123	83.03
					1.0		230	87	83.82

TABLE 2

Precursor	Solvent			Reducing	Protective			Volume	Copper	Standard deviation	
Copper isostearate (g)	Anhydrous alcohol (mL)	Methanol (mL)	Ethylene glycol (mL)	agent Vitamin C (g)	agent PVP (g)	Reaction temperature (° C.)	CO_2 pressure (psi)	expansion rate (ΔV/V)/%	average particle size (nm)	of copper particle size	Conversion rate (%)
1	10	10	10	0.5	0.5	30	0	0	205	56	81.54
							500	16.67	255	95	96.94
							600	26.67	210	71	97.2
							700	33.33	201	83	99.16
							800	40	186	59	99.5
							900	50	183	77	99.4
							1000	83.33	176	64	99.6

[0031] Next, the nano copper suspension solution was centrifuged at 6000 rpm for half an hour to make nano copper precipitate at the bottom of the centrifuge tube. After the solvent in the upper layer in which impurities were dissolved was discarded, the nano copper was placed in a vacuum oven for 1 hour to obtain nano copper chunks. After weighing, anhydrous alcohol and tert-butanol in a volume ratio of 1:2 were added to form 20 wt % of copper ink. The preparation of copper ink was performed by mixing ethylene glycol and anhydrous alcohol at different ratios, and the resistivity thereof after spin coating (1500 rpm) and 250° C. sintering is shown in Table 3 (four-point probe detection). If the ethylene glycol ratio was higher, then the film after spin coating was not continuous, wherein the resistivity of anhydrous alcohol and ethylene glycol (3:2) was lowest. The resulting copper ink was sintered at different temperatures (200° C., 250° C., 300° C., 350° C., and 400° C.) after spin coating, wherein conductivity started to occur at 250° C., and conductivity was best at 400° C.

TABLE 3

Ink recipe	Sintering temperature (° C.)	Sheet resistance (Ω/□)	Film thickness (nm)	Resistivity (Ω · m)
20 wt % Cu and ethylene glycol	250		N/A	
20 wt % Cu, anhydrous alcohol, and ethylene glycol (1:4)			N/A	
20 wt % Cu, anhydrous alcohol, and ethylene glycol (2:3)		61	355	2.2×10^{-5}
20 wt % Cu, anhydrous alcohol, and ethylene glycol (3:2)		25	316	7.9×10^{-6}
20 wt % Cu, anhydrous alcohol, and ethylene glycol (4:1)		111	249	2.8×10^{-5}
20 wt % Cu and anhydrous alcohol		934	106	9.9×10^{-5}

[0032] Based on the above, the invention provides a conductive ink containing nano copper powders having a small particle size with copper isostearate as the precursor and containing a reducing agent a protective agent, wherein the copper isostearate is formed by the reduction reaction of isostearic acid and a copper-containing compound. Via the conductive ink of the invention, a conductive layer having a smaller thickness (such as 1 μm or less) and good conductivity can be formed, and advantages of simple preparation method (coating method) and low cost are obtained, so the current development trend of a compact and lightweight product is met.

[0033] Although the invention has been described with reference to the above embodiments, it will be apparent to one of ordinary skill in the art that modifications to the described embodiments may be made without departing from the spirit of the invention. Accordingly, the scope of the invention is defined by the attached claims not by the above detailed descriptions.

1. A conductive ink, comprising:

a precursor comprising copper isostearate ($Cu(C_{18}H_{36}O_2)_2$);

a reducing agent; and

a protective agent,

wherein based on a total weight of the conductive ink, a content of the precursor is 40 wt % to 75 wt %, a content of the reducing agent is 20 wt % to 32 wt %, and a content of the protective agent is 5 wt % to 40 wt %.

2. The conductive ink of claim **1**, further comprising a solvent.

3. The conductive ink of claim **2**, wherein the solvent comprises water, toluene, cyclohexane, n-heptane, isooctane, methanol (MeOH), ethanol (EtOH), ethylene glycol (EG), diethylene glycol, or supercritical carbon dioxide.

4. The conductive ink of claim **1**, wherein the reducing agent comprises Vitamin C, sodium borohydride ($NaBH_4$), hydrazine (N_2H_4), hydrogen peroxide (H_2O_2), hydrogen (H_2), sodium hypophosphite (NaH_2PO_2), sodium citrate ($Na_3C_6H_5O_7$), potassium sodium tartrate ($NaKC_4H_4O_6$), an amine compound, or an aldehyde compound.

5. The conductive ink of claim **4**, wherein the amine compound comprises dimethylformamide (DMF).

6. The conductive ink of claim **4**, wherein the aldehyde compound comprises glucose.

7. The conductive ink of claim **1**, wherein the protective agent comprises polyacrylic acid (PAA), polyvinyl alcohol (PVA), polyvinylpyrrolidone (PVP), gelatin, sodium dodecyl sulfate (SDS), polyethylene glycol octylphenyl ether (TX-100), cetyltrimethylammonium bromide (CTAB), sodium dioctyl sulfosuccinate (AOT), bis(2-ethylhexyl) phosphoric acid (HDEHP), oleic acid, or dodecaneamine.

8. The conductive ink of claim **1**, wherein the precursor is formed by a reduction reaction of isostearic acid ($C_{18}H_{36}O_2$) and a copper-containing compound.

9. The conductive ink of claim **8**, wherein the copper-containing compound comprises $CuSO_4$, $CuCl_2$, $Cu(AOT)_2$, $Cu(NO_3)_2$, $Cu(OH)_2$, or $Cu(acac)_2$.

* * * * *