

Metal Ink Compositions, Conductive Patterns, Methods, and Devices

RELATED APPLICATIONS

This application claims priority to US provisional application serial no. 61/259,614 filed on November 9, 2009, which is hereby incorporated by reference in its entirety.

INTRODUCTION

Printed electronics is projected to be a multi-billion business within the next 7-10 years, with the inks alone constituting 10-15% of the dollar amount, according to some sources. The increased interest in printable electronics as rapidly growing alternatives to silicon-based technologies is fueled by, among other things, the promise of large-area, flexible, lightweight and low-cost devices.

More particularly, a need exists for better methods for printing metals such as, for example, copper, silver, and gold. These metals are important chip components ranging from interconnects to organic field effect transistor source and drain electrodes. In general, improved compositions and methods for producing metal structures are needed, particularly for commercial applications and inkjet printing. See, for example, U.S. Patent Nos. 7,270,694; 7,443,027; 7,491,646; 7,494,608 (assignee: Xerox); US Patent Publication 2010/0163810 ("Metal Inks"); US Patent Publication 2008/0305268 ("Low Temperature Thermal Conductive Inks"); and US Patent Publication 2006/0130700 ("Silver Containing Inkjet Inks").

SUMMARY

Provided herein are compositions, devices, methods of making compositions and devices, and methods of using compositions and devices, among other embodiments.

One embodiment (Embodiment A) provides, for example, a composition comprising at least one metal complex comprising at least one metal and at least two ligands, wherein at least one first ligand is a sigma donor to the metal and volatilizes upon heating the metal complex, and at least one second ligand different from the first which also volatilizes upon heating the metal complex, wherein the metal complex is soluble in a solvent at 25°C. Methods of making, formulating, and using this composition also are provided for embodiment A and sub-embodiments thereof.

In one embodiment, the metal is silver, gold, copper, platinum, or ruthenium.

In one embodiment, the metal is silver, gold, or copper.

In one embodiment, the metal is silver or gold.

In one embodiment, the metal complex comprises only one metal center.

In one embodiment, the metal is in an oxidation state of (I) or (II).

In one embodiment, the first ligand is a monodentate ligand.

In one embodiment, the first ligand is a bidentate ligand.

In one embodiment, the first ligand is a tridentate ligand.

In one embodiment, the first ligand is an amine compound comprising at least two nitrogen.

In one embodiment, the first ligand is an unsymmetrical amine compound comprising at least two nitrogen.

In one embodiment, the first ligand is tetrahydrothiophene or an amine.

In one embodiment, the first ligand is a thioether. The thioether can be cyclic or linear.

In one embodiment, the first ligand is not a phosphine.

In one embodiment, the second ligand is a carboxylate.

In one embodiment, the second ligand is a carboxylate comprising an alkyl group.

In one embodiment, the second ligand is a carboxylate represented by -OOC-R , wherein R is an alkyl group, wherein R has 10 or fewer carbon atoms.

In one embodiment, the second ligand is a carboxylate represented by OOC-R , wherein R is an alkyl group, wherein R has 5 or fewer carbon atoms.

In one embodiment, the composition is substantially free of nanoparticles.

In one embodiment, the composition is totally free of nanoparticles.

In one embodiment, the composition has a sharp decomposition transition beginning at a temperature of less than 200°C .

In one embodiment, the composition has a sharp decomposition transition beginning at a temperature of less than 150°C .

In one embodiment, the composition can be stored at about 25°C for at least 100 hours without substantial deposition of metal (0).

In one embodiment, the composition further comprises at least one solvent for the complex.

In one embodiment, the composition further comprises at least one aromatic hydrocarbon solvent.

In one embodiment, the composition further comprises at least one solvent, and the concentration of the complex is about 200 mg/mL or less.

In one embodiment, the solvent is an aromatic hydrocarbon solvent.

In one embodiment, the metal complex comprises at least 25 wt.% metal.

In one embodiment, the metal complex comprises at least 50 wt.% metal.

In one embodiment, the metal complex comprises at least 70 wt.% metal.

In one embodiment, the second ligand is a carboxylate, and the first ligand is a polydentate amine, and the metal is silver, gold, or copper.

In one embodiment, the second ligand is a carboxylate, the first ligand is a polydentate unsymmetrical amine, the metal is silver or gold, and wherein the solvent is toluene.

Another embodiment (Embodiment B) provides a composition comprising at least one metal complex comprising at least one metal and at least two ligands, wherein at least one first ligand is a sulfur-containing ligand, and at least one second ligand different from the first which, optionally, is a carboxylate, wherein the metal complex is soluble in a solvent at 25°C. Methods of making, formulating, and using this composition also are provided for Embodiment B and sub-embodiments thereof. The composition can be substantially free of nanoparticles.

In one embodiment, the second ligand is a carboxylate; i.e., the carboxylate is not optional.

In one embodiment, the content of metal in the complex is at least 50 wt.%.

In one embodiment, the sulfur-containing ligand is a thioether ligand. The thioether can be cyclic or linear.

In one embodiment, the sulfur containing ligand is tetrahydrothiophene.

In one embodiment, the sulfur-containing ligand is a dialkylthioether.

In one embodiment, the sulfur-containing ligand is a dithiaalkane.

In one embodiment, the sulfur-containing ligand is a dithioctane.

In one embodiment, the sulfur-containing ligand comprises one or two sulfur atoms.

In one embodiment, the sulfur-containing ligand is a bidentate ligand.

In one embodiment, the sulfur-containing ligand has six carbons or less, or four carbons or less, or two carbons or less.

Another embodiment (Embodiment C) provides a composition comprising at least one metal complex comprising at least one metal and at least two ligands, wherein at least one first ligand is an amino ligand, and at least one second ligand different from the first which, optionally, is a carboxylate, wherein the metal complex is soluble in a solvent at 25°C. Methods of making, formulating, and using this composition also are provided for

Embodiment C and sub-embodiments thereof. The composition can be substantially free of nanoparticles.

Another embodiment provides that the content of metal in the complex is at least 50 wt.%.

Another embodiment provides the second ligand is a carboxylate.

Another embodiment provides the metal is silver, gold, copper, platinum, or ruthenium.

Another embodiment provides the metal complex comprises only one metal center.

Another embodiment provides the metal is in an oxidation state of (I) or (II).

Another embodiment provides the first ligand is a monodentate ligand.

Another embodiment provides the first ligand is a bidentate ligand.

Another embodiment provides the first ligand is a tridentate ligand.

Another embodiment provides the first ligand is an unsymmetrical amino ligand comprising at least two nitrogen.

Another embodiment provides the first ligand is an unsymmetrical amino ligand comprising at least two nitrogen.

Another embodiment (Embodiment D) provides a composition comprising at least one neutral metal complex comprising at least one metal in a (I) or (II) oxidation state, and at least two ligands, wherein at least one first ligand is a neutral sigma donor to the metal and volatilizes upon heating the metal complex to a temperature below 150°C, and at least one second anionic ligand different from the first which also volatilizes upon heating the metal complex to a temperature below 150°C, wherein, optionally, the metal complex is soluble in a solvent at 25°C. Methods of making, formulating, and using this composition also are provided for Embodiment D and sub-embodiments thereof.

Another embodiment provides the first ligand is a sulfur-containing ligand.

Another embodiment provides the first ligand is tetrahydrothiophene.

Another embodiment provides the first ligand is a thioether. The thioether can be cyclic or linear.

Another embodiment provides the first ligand comprises at least two sulfurs.

Another embodiment provides the first ligand has six or fewer carbon atoms.

Another embodiment provides the first ligand has four or fewer carbon atoms.

Another embodiment provides the first ligand has two or fewer carbon atoms.

Another embodiment provides the first ligand second ligand is a carboxylate.

Another embodiment provides the number of carbon atoms in the complex is twelve or less.

Another embodiment provides a method comprising: depositing an ink on a surface, wherein the ink comprises a composition according to embodiments described herein, and producing a conductive metal film by heating or irradiating said ink.

In one embodiment, the producing step is carried out by heating.

In one embodiment, the producing step is carried out by irradiating.

In one embodiment, the ink comprises a composition according to Embodiment A and sub-embodiments thereof.

In one embodiment, the ink comprises a composition according to Embodiment B and sub-embodiments thereof.

In one embodiment, the ink comprises a composition according to Embodiment C and sub-embodiments thereof.

In one embodiment, the ink comprises a composition according to Embodiment D and sub-embodiments thereof.

In one embodiment, the metal is gold, silver, or copper.

In one embodiment, the ink is substantially free of nanoparticles before deposition.

In one embodiment, the ink is substantially free of nanoparticles after deposition.

In one embodiment, the depositing is carried out by inkjet deposition.

In one embodiment, the producing is carried out by heating at a temperature of about 250°C or less.

In one embodiment, the producing is carried out by heating at a temperature of about 200°C or less.

In one embodiment, the producing is carried out by heating at a temperature of about 150°C or less.

In one embodiment, the film is in the form of a line, and the line has a conductivity of at least 1,000 S/cm.

In one embodiment, the film is in the form of a line, and the line has a conductivity of at least 5,000 S/cm.

In one embodiment, the film is in the form of a line, and the line has a conductivity of at least 10,000 S/cm.

In one embodiment, the film is in the form of a line, and the line has a work function which is within 25 percent of the work function of the pure metal.

In one embodiment, the film is in the form of a line, and the line has a work function which is within 10 percent of the work function of the pure metal.

In one embodiment, the film is in the form of a line, and the line has a work function which is within 5 percent of the work function of the pure metal..

Another embodiment provides a method comprising: depositing an ink on a surface to form a deposit, converting the deposit to a metal film, wherein the metal film shows a work function which is within 25 percent of the work function of the pure metal.

In one embodiment, the deposit is heated.

In one embodiment, the deposit is irradiated.

In one embodiment, the ink comprises a composition according to embodiments described herein.

In one embodiment, the ink comprises a composition according to Embodiment A and sub-embodiments thereof.

In one embodiment, the ink comprises a composition according to Embodiment B and sub-embodiments thereof.

In one embodiment, the ink comprises a composition according to Embodiment C and sub-embodiments thereof.

In one embodiment, the ink comprises a composition according to Embodiment D and sub-embodiments thereof.

In one embodiment, the metal is gold, silver, or copper.

In one embodiment, the ink is substantially free of nanoparticles before deposition.

In one embodiment, the ink is substantially free of nanoparticles after deposition.

In one embodiment, the depositing is carried out by inkjet deposition.

In one embodiment, the converting is carried out by heating at a temperature of about 250°C or less.

In one embodiment, the converting is carried out by heating at a temperature of about 200°C or less.

In one embodiment, the converting is carried out by heating at a temperature of about 150°C or less.

In one embodiment, the film is in the form of a line, and the line has a conductivity of at least 1,000 S/cm.

In one embodiment, the film is in the form of a line, and the line has a conductivity of at least 5,000 S/cm.

In one embodiment, the film is in the form of a line, and the line has a conductivity of at least 10,000 S/cm.

In one embodiment, the film is in the form of a line, and the line has a work function which is within 10 percent of the work function of the pure metal.

In one embodiment, the film is in the form of a line, and the line has a work function which is within 5 percent of the work function of the pure metal.

Another embodiment provides a composition comprising at least one metal complex comprising at least one metal and at least two ligands, wherein at least one first ligand is a sigma donor to the metal and volatilizes upon heating the metal complex, and at least one second ligand which also volatilizes upon heating the metal complex, wherein the metal complex is soluble in a solvent at 25°C.

In one embodiment, the first ligand and the second ligand are the same ligand.

In one embodiment, the first ligand and the second ligand are different ligands.

In one embodiment, the metal is copper. In other embodiments, the metal can also be, for example, silver, gold, platinum, or ruthenium.

In one embodiment, the first ligand comprises at least one nitrogen atom and at least two oxygen atoms.

In one embodiment, the first ligand and the second ligand are the same ligand, and wherein the first ligand comprises at least one nitrogen atom and at least two oxygen atoms.

In one embodiment, the first ligand and the second ligand are the same ligand, and wherein the first ligand comprises at least one nitrogen atom and at least two oxygen atoms, as well as at least one fluorine.

In one embodiment, the first ligand is a tridentate ligand.

In one embodiment, the first ligand is a tridentate Schiff base ligand.

In one embodiment, the first ligand comprises at least one secondary amine group, at least one carbonyl group, and at least one ether group.

In other embodiments, the compositions consist essentially of ingredients and components described herein.

Another embodiment provides a composition comprising at least one metal complex comprising at least one metal and at least two ligands, wherein at least one first ligand is a sigma donor to the metal and volatilizes upon heating the metal complex to a temperature of about 250°C or less, and at least one second ligand, which is optionally different from the first, which also volatilizes upon heating the metal complex to a temperature of about 250°C or less.

In one embodiment, the metal complex is heated to a temperature of 150°C or less.

In one embodiment, the metal complex is soluble at 25°C.

In one embodiment, the composition upon heating provides a metal with a work function which is within 25 percent of the work function of the pure metal.

In one embodiment, the composition upon heating provides a metal composition having a conductivity of at least 1,000 S/cm.

Another embodiment provides a method comprising: depositing an ink on a surface to form a deposit, converting the deposit to a metal film, wherein the metal film shows a conductivity of at least 1,000 S/cm.

Another embodiment provides that the conductivity is at least 5,000 S/cm.

Another embodiment provides that the conductivity is at least 10,000 S/cm.

Another embodiment provides that the converting is carried out by heating at a temperature of about 200°C or less.

Another embodiment provides that the converting is carried out by heating at a temperature of about 150°C or less.

Still further, another embodiment is a composition comprising at least one metal complex consisting essentially of at least one metal and at least two ligands bonded to the metal, wherein at least one first ligand is a neutral donor to the metal and volatilizes upon heating the metal complex, and at least one second ligand different from the first which also volatilizes upon heating the metal complex and is negatively charged.

Another embodiment provides that the first ligand consists essentially of nitrogen and/or sulfur.

Another embodiment provides that the second ligand consists essentially of a carboxylate.

Another embodiment provides that the complex is soluble in toluene.

Another embodiment provides that the complex consisting essentially of the metal, the first ligand, and the second ligand is neutrally charged.

At least one advantage for at least one embodiment is ability to make useful conductive metal lines and films of high quality. At least one additional advantage for at least one embodiment is the low temperature nature of the conversion to conductive metal. At least one additional advantage for at least one embodiment is the high metal content of the metal inks. At least one additional advantage for at least one embodiment is the high conductivity of metal films. Furthermore, at least one additional advantage for at least one embodiment is ability to be inkjet printed.

Other advantages for at least some embodiments include aspects described below.

BRIEF DESCRIPTION OF FIGURES

Figure 1 illustrates one embodiment, showing a diffraction-derived molecular structure of a gold complex.

Figure 2 illustrates one embodiment in a perspective view, showing an AFM image of well-separated Au nanoparticles in a triphenylphosphine oxide matrix.

Figure 3 illustrates one embodiment, showing a thermogravimetric analysis of a gold complex.

Figure 4 illustrates one embodiment, showing a diffraction-derived molecular structure of a dinuclear silver complex.

Figure 5 illustrates one embodiment, showing a diffraction-derived molecular structure of a mononuclear silver complex.

Figure 6 illustrates one embodiment, showing the log resistivity versus temperature plot of a (DEED)Ag(isobutyrate) line drawn between two gold electrode pads on Si/SiO₂ from a 65 mg/mL toluene solution.

Figure 7 illustrates one embodiment in a top view, showing a scanning electron microscopy image of deposited metallic silver.

Figure 8 illustrates one embodiment, showing energy dispersive x-ray spectroscopy of deposited metallic silver.

Figure 9 illustrates one embodiment in a top view, showing an inkjet deposition of silver ink.

Figure 10 illustrates one embodiment, showing the log resistivity (arbitrary units) versus temperature plot (°C) of a (DEED)Ag(cyclopropate) line drawn between two gold electrode pads on Si/SiO₂ from a 65 mg/mL toluene solution.

Figure 11 illustrate one embodiment, showing the log resistivity (arbitrary units) versus temperature (°C) plot of a (PMDEA)Ag(isobutyrate) line drawn between two gold electrode pads on Si/SiO₂ from a 65 mg/mL toluene solution.

Figure 12 illustrate one embodiment, showing the log resistivity (arbitrary units) versus temperature (°C) plot of a copper complex.

Figure 13 illustrates one embodiment in a top view, showing a scanning electron microscopy image of copper lines drawn on a SiO₂ substrate.

Figure 14 illustrates one embodiment, showing energy dispersive x-ray spectroscopy of copper lines drawn on a SiO₂ substrate.

Figure 15 illustrates one embodiment, showing a diffraction-derived molecular structure of a silver complex.

Figure 16 illustrates one embodiment, showing XPS of Au film formed from precursor solution and evolution with sputtering cleaning steps for Au4f, Ag3d, C1s, and O1s.

Figure 17 illustrates one embodiment, showing work function of Au from the precursor (4.9 eV).

Figure 18 illustrates one embodiment, showing a diffraction-derived molecular structure of a silver complex.

Figure 19 illustrates one embodiment, showing the log resistivity (arbitrary units) versus temperature (°C) plot of a silver line drawn between two gold electrode pads.

Figure 20 illustrates one embodiment in a top view, showing a image of a silver line drawn between two gold electrode pads.

Figure 21 illustrates one embodiment, showing procedures of synthesizing of gold complexes.

Figure 22 illustrates one embodiment in a perspective view, showing a micro-casting setup.

Figure 23 illustrates one embodiment, showing the log resistivity (arbitrary units) versus temperature (°C) plot for metallization of gold solution.

Figure 24 illustrates one embodiment in a top view, showing a (low resolution) scanning electron microscopy image of a gold line drawn between two gold electrode pads prepared by lithography.

Figure 25 illustrates one embodiment, showing energy dispersive x-ray spectroscopy of a gold line drawn between two gold electrode pads.

Figure 26 illustrates one embodiment in a top view, showing inkjet printed gold lines.

Figure 27 illustrates one embodiment, comparing XPS Au peaks for Au films prepared from (A) precursor solution and (B) using sputter deposition.

Figure 28 illustrates one embodiment, showing conductivity from liquid gold.

Figure 29 illustrates one embodiment, showing diffraction-derived molecular structure of a trinuclear gold complex.

Figures include, in some cases, color figures and features, and the color features form part of the disclosure.

DETAILED DESCRIPTION

INTRODUCTION

Priority US provisional application serial no. 61/259,614 filed on November 9, 2009 is hereby incorporated by reference in its entirety.

Microfabrication, printing, ink jet printing, electrodes, and electronics are described in, for example, Madou, *Fundamentals of Microfabrication*, The Science of Miniaturization, 2nd Ed., 2002.

Organic chemistry methods and structures are described in, for example, March's *Advanced Organic Chemistry*, 6th Ed., 2007.

To help enable the growing demands of printing processes and other applications, new metal-containing inks are provided herein for the solution-based deposition of conductive metal films, including coinage metal films, including, for example, copper, silver, and gold films. The metallizing ink approach provided herein is based on coordination chemistry and self-reducing ligands that can be, for example, heated or photochemically irradiated to yield metallic films.

Patterning methods including, for example, inkjet printing, can be employed to deposit the metal inks in specific, predetermined patterns which can be directly transformed into, for example, circuitry using a laser or simple heating, including low temperature heating.

The versatility of this approach provides printing a variety of designs and patterns on a variety of substrates for much cheaper than conventional deposition methods without the need for lithography.

Herein, a composition can comprise at least one metal complex, as well as optional other components including, for example, solvent. In one embodiment, the composition does not comprise a polymer. In one embodiment, the composition does not comprise a surfactant. In one embodiment, the composition comprises only metal complex and solvent.

In formulating compositions, examples of prerequisite synthetic criteria include, for example: (1) compounds can be air- and moisture stable, (2) compounds can show longevity and can be stored for long periods or indefinitely, (3) synthesis of the compounds is amenable to the large scale while being inexpensive with high yields, (4) compounds are soluble in aromatic hydrocarbons, such as toluene and xylenes, which are compatible with printing processes such as inkjet and Patch pipette, and/or (5) compounds should cleanly decompose, either thermally or photochemically, to base metal.

METAL COMPLEX

The metal complex can be a precursor to a metal film. Metal organic and transition metal compounds, metal complexes, metals, and ligands are described in, for example, Lukehart, *Fundamental Transition Metal Organometallic Chemistry*, Brooks/Cole, 1985; Cotton and Wilkinson, *Advanced Inorganic Chemistry: A Comprehensive Text*, 4th Ed., John Wiley, 2000. The metal complex can be homoleptic or heteroleptic. The metal complex can be mononuclear, dinuclear, trinuclear, and higher. The metal complex can be a covalent complex.

The metal complex can be free from metal-carbon bonding.

The metal complex can be as a whole uncharged so there is not a counterion which is not directly bonding to the metal center. For example, in one embodiment, the metal complex is not represented by $[M]^+[A]^-$ wherein the metal complex and its ligands are a cation. In one embodiment, the metal complex can be represented by ML_1L_2 , wherein L_1 and L_2 are the first and second metal ligands, respectively. M here may have a positive charge which is balanced by a negative charge from L_1 or L_2 .

The metal complex can be free from anions such as halide, hydroxide, cyanide, nitrite, nitrate, nitroxyl, azide, thiocyanato, isothiocyanato, tetraalkylborate, tetrahaloborate, hexafluorophosphate, triflate, tosylate, sulfate, and/or carbonate.

In one embodiment, the metal complex is free of fluorine atoms, particularly for silver and gold complexes.

The composition comprising the metal complex can be substantially or totally free of particles, microparticles, and nanoparticles. In particular, the composition comprising the metal complex can be substantially or totally free of nanoparticles including metal nanoparticles, or free of colloidal material. See, for example, US Patent No. 7,348,365 for colloidal approaches to form conductive inks. For example, the level of nanoparticles can be less than 0.1 wt.%, or less than 0.01 wt.%, or less than 0.001 wt. %. One can examine composition for particles using methods known in the art including, for example, SEM and TEM, spectroscopy including UV-Vis, plasmon resonance, and the like. Nanoparticles can have diameters of, for example, 1 nm to 500 nm, or 1 nm to 100 nm.

The composition comprising the metal complex can be also free of flakes.

In some embodiments, the composition can comprise at least two different metal complexes.

The metal complexes can be also adapted for use in forming materials like oxides and sulfides, including ITO and ZnO.

In one embodiment, the metal complex is not an alkoxide such as a copper alkoxide (e.g., absence of M-O-R linkage).

SOLUBILITY

The metal complex can be soluble, which facilitates further processing. It can be soluble in, for example, in a non-polar or less polar solvent such as a hydrocarbon, including an aromatic hydrocarbon solvent. Aromatic hydrocarbon solvent includes benzene and toluene. Another example is a xylene or mixtures of xylenes. Polyalkylaromatics can be used.

The composition comprising metal complex can further comprise at least one solvent for the complex including at least one aromatic hydrocarbon solvent. An oxygenated solvent can be substantially or totally excluded including, for example, water, alcohols, glycols including ethylene glycol, polyethers, aldehydes, and the like.

The composition comprising metal complex can further comprise at least one solvent, and the concentration of the complex can be about 200 mg/mL or less, or about 100 mg/mL or less, or about 50 mg/mL or less.

In one embodiment, the metal complex is used without a solvent.

In one embodiment, the composition is free of, or substantially free of water. For example, the amount of water can be less than 1 wt.%. Or, the amount of water can be less than 0.1 wt.% or less than 0.01 wt.%.

In one embodiment, the composition is free of, or substantially free of oxygenated solvent. For example, the amount of oxygenated solvent can be less than 1 wt.%. Or, the amount of oxygenated solvent can be less than 0.1 wt.% or less than 0.01 wt.%.

METAL CENTER

Metals and transition metals are known in the art. See, for example, Cotton and Wilkinson text, cited above. Coinage metals can be used including silver, gold, and copper. Platinum can be used. Nickel, cobalt, and palladium can be used. Lead, iron, and tin can be used, for example. Ruthenium can be used. Other examples of metals used for conductive electronics are known and can be used as appropriate. Mixtures of metal complexes with different metals can be used. Alloys can be formed.

The metal complex can comprise only one metal center. Or the metal complex can comprise only one or two metal centers.

The metal can be in an oxidation state of (I) or (II).

The metal center can be complexed with first and second ligands. Additional ligands, third, fourth, and the like can be used.

The metal center can be complexed at multiple sites including complexed with three, four, five, or six complexing sites.

The metal center can comprise a metal useful for forming electrically conducting lines, particularly those metals used in the semiconductor and electronics industries.

Still other examples of metals include indium and tin.

FIRST LIGAND

The first ligand can provide sigma electron donation, or dative bonding, to the metal. Sigma donation is known in the art. See, for example, US Patent No. 6,821,921. The first ligand can be adapted to volatilize when heated without formation of a solid product. Heating can be done in the presence or absence of oxygen. The first ligand can be a reductant for the metal. The first ligand can be in neutral state, not an anion or a cation.

The first ligand can be a polydentate ligand including, for example, a bidentate or a tridentate ligand.

The first ligand can be an amine compound comprising at least two nitrogen. The ligand can be symmetrical or unsymmetrical.

The first ligand can be an unsymmetrical amine compound comprising at least two nitrogen.

The first ligand can be, for example, a ligand comprising sulfur, such as tetrahydrothiophene, or an amine. Amine ligands are known in the art. See, for example, Cotton and Wilkinson textbook cited above, page 118. Also, nitrogen heterocycles like pyridine can be used.

The first ligand can be an amine including an alkyl amine. The alkyl groups can be linear, branched, or cyclic. Bridging alkylene can be used to link multiple nitrogen together. In the amine, the number of carbon atoms can be, for example, 15 or less, or ten or less.

The molecular weight of the first ligand, including an amine, can be, for example, about 1,000 g/mol or less, or about 500 g/mol or less, or about 250 g/mol or less.

In one embodiment, the first ligand is not a phosphine. In one embodiment, the first ligand is not tetrahydrothiophene. In one embodiment, the first ligand does not comprise a ligand comprising sulfur. In one embodiment, the first ligand does not comprise an amine. In one embodiment, the first ligand does not comprise a fluorine-containing ligand.

Examples of the first ligand can be found in the working examples below.

SECOND LIGAND

The second ligand is different from the first ligand and can volatilizes upon heating the metal complex. For example, it can release carbon dioxide, as well as volatile small organic molecules, in some embodiments. The second ligand can be adapted to volatilize when heated without formation of a solid product. Heating can be done in the presence or absence of oxygen. The second ligand can be a chelators with a minimum number of atoms that can bear an anionic charge and provide a neutral complex. This can make the complex soluble in aromatic hydrocarbon solvent. The second ligand can be anionic. It can be self-reducing.

The second ligand can be a carboxylate, which is known in the art. See, for example, Cotton and Wilkinson textbook cited above, pages 170-172. Carboxylates including silver carboxylates are known in the art. See, for example, US Patent Nos. 7,153,635; 7,445,884; 6,991,894; and 7,524,621.

The second ligand can be a carboxylate comprising a hydrocarbon such as, for example, an alkyl group.

The second ligand can be a carboxylate represented by OOC-R , wherein R is an alkyl group, wherein R has 10 or fewer carbon atoms, or five or fewer carbon atoms. R can be linear, branched, or cyclic. The second ligand can be fluorinated if desired including, for example, comprise trifluoromethyl groups. The second ligand can be a carboxylate but not a fatty acid carboxylate. The second ligand can be an aliphatic carboxylate. The second ligand can be not a formate ligand.

The molecular weight of the second ligand, including the carboxylate, can be, for example, about 1,000 g/mol or less, or about 500 g/mol or less, or about 250 g/mol, or about 150 g/mol or less or less.

In one embodiment, the second ligand does not comprise a fluorine-containing ligand.

Examples of the second ligand can be found in the working examples below.

AN ADDITIONAL EMBODIMENT

In another embodiment, the metal complex can comprise at least two ligands, comprising first and second ligands, and the ligands can be the same or different.

In particular, another embodiment provides a composition comprising at least one metal complex comprising at least one metal and at least two ligands, wherein at least one first ligand is a sigma donor to the metal and volatilizes upon heating the metal complex, and

at least one second ligand which also volatilizes upon heating the metal complex. The metal complex can be soluble in a solvent at 25°C.

In one embodiment, the first ligand and the second ligand are the same ligand. In one embodiment, the first ligand and the second ligand are different ligands.

In one embodiment, the metal is copper. In other embodiments, the metal can also be, for example, silver, gold, platinum, or ruthenium.

In one embodiment, the first ligand comprises at least one nitrogen atom and at least two oxygen atoms.

In one embodiment, the first ligand and the second ligand are the same ligand, and the first ligand comprises at least one nitrogen atom and at least two oxygen atoms.

In one embodiment, the first ligand and the second ligand are the same ligand, and wherein the first ligand comprises at least one nitrogen atom and at least two oxygen atoms, as well as at least one fluorine. For example, the fluorine can be part of a trifluoromethyl group.

In one embodiment, the first ligand is a tridentate ligand. In one embodiment, the first ligand is a tridentate Schiff base ligand.

In one embodiment, the first ligand comprises at least one secondary amine group, at least one carbonyl group, and at least one ether group.

See, for example, for this additional embodiment, working example 6 below and the ligand used therein as first and second ligand.

CHARACTERISTICS OF THE METAL COMPLEXES

The metal complex can have a sharp decomposition transition beginning at a temperature of less than 250°C, or less than 200°C, or less than 150°C, or less than 120°C.

The composition can be stored at about 25°C for at least 100 hours, or at least 250 hours, or at least 500 hours, or at least 1,000 hours, or at least six months, without substantial deposition of metal (0). This storage can be neat or in a solvent. The composition can be stored at lower temperatures such as, for example, less than 25°C to provide longer stability. For example, some composition can be stored at 0°C for very long periods of time including, for example, at least 30 days, or at least 90 days, or at least 365 days. Alternatively, for example, some composition can be stored at -35°C or lower for very long periods of time including, for example, at least 30 days, or at least 90 days, or at least 365 days.

The complexes can comprise, for example, at least 25 wt.% metal, or at least 50 wt.% metal, or at least 60 wt.% metal, or at least 70 wt.% metal. This provides for efficient use of metal and good conductivity upon conversion to metal.

The metal complexes can be adapted to provide sufficient stability to be commercially useful, but also sufficiently reactive to provide low cost, high quality products. One skilled in the art can adapt the first and second ligands to achieve a balance needed for a particular application.

METHODS OF MAKING COMPOSITIONS

Metal complexes can be made by a variety of methods. In one embodiment, metal or silver carboxylate complexes are prepared by reacting the metal or silver carboxylate precursor with an ester so that an exchange reaction occurs to form a new metal or silver carboxylate complex. See, for example, reaction (1) below, wherein R can be, for example, an alkyl group including a linear, branched, or cyclic alkyl, including for example an alkyl group with ten or fewer, or five or fewer carbon atoms. The yield of reaction can be, for example, at least 50%, or at least 70%, or at least 90%.

In one embodiment, the metal or silver carboxylate complex is made without use of metal oxide including Ag_2O . In one embodiment, the metal or silver carboxylate is made without use of a solid state reaction. See, for example, comparative example reaction (2) below.

In one embodiment, gold complexes are prepared by reaction of a gold chloride complex, which is also complexed with a sigma donor such as tetrahydrothiophene or a phosphine, with a silver carboxylate complex. The result is precipitation of silver chloride. See, for example, reactions (3), (4), and (5) below.

In one embodiment, metal complexes are prepared by exchanging dative bonding ligands such as the first ligands. For example, tetrahydrothiophene can be exchanged for an amine.

DEPOSITION OF INK

Methods known in the art can be used to deposit inks including, for example, spin coating, pipetting, inkjet printing, blade coating, rod coating, dip coating, lithography or offset printing, gravure, flexography, screen printing, stencil printing, drop casting, slot die, roll-to-roll, spraying, and stamping. One can adapt the ink formulation and the substrate with the deposition method. See also *Direct Write Technologies* book cited above. For example,

chapter 7 describes inkjet printing. Contact and non-contact deposition can be used. Vacuum deposition can be not used. Liquid deposition can be used.

One can adapt the viscosity of the ink to the deposition method. For example, viscosity can be adapted for ink jet printing. Viscosity can be, for example, about 500 Cps or less. Or viscosity can be, for example, 1,000 Cps or more. One can also adapt the concentration of solids in the ink. The concentration of the solids in the ink can be, for example, about 500 mg/mL or less, or about 250 mg/mL or less, or about 100 mg/mL or less, or about 150 mg/mL or less, or about 100 mg/mL or less. A lower amount can be, for example, about 1 mg/mL or more, or about 10 mg/mL or more. Ranges can be formulated with these upper and lower embodiments including, for example, about 1 mg/mL to about 500 mg/mL. In addition, the wetting properties of the ink can be adapted.

Additives such as, for example, surfactants, dispersants, and/or binders can be used to control one or more ink properties if desired. In one embodiment, an additive is not used. In one embodiment, a surfactant is not used.

Nozzles can be used to deposit the precursor, and nozzle diameter can be, for example, less than 100 microns, or less than 50 microns. The absence of particulates can help with prevention of clogging the nozzle.

In deposition, solvent can be removed, and the initial steps for converting metal precursor to metal can be started.

CONVERTING PRECURSOR TO METAL

The inks and compositions comprising metal complexes can be deposited and converted to metallic structures including films and lines. Heat and/or light can be used including laser light. The atmosphere around the metal film can be controlled. For example, oxygen can be included or excluded. Volatile by-products can be eliminated.

METALLIC LINES AFTER DEPOSITION AND CURING

The metallic lines and films can be coherent and continuous. Continuous metallization can be observed with good connectivity between grains and low surface roughness.

Line width can be, for example, 1 micron to 500 microns, or 5 microns to 300 microns. Line width can be less than one micron if nanoscale patterning methods are used.

Dots or circles can be also made.

In one embodiment, ink formulations can be converted to metallic lines and films without formation of substantial amounts of metal particles, microparticles, or nanoparticles.

Metal lines and films can be prepared with characteristics of metal and lines prepared by other methods like sputtering.

Metal lines and films can be, for example, at least 90 wt.% metal, or at least 95 wt.% metal, or at least 98 wt.% metal.

Metal lines and films can be relative smooth according to AFM measurements.

Metal lines and films can be used to join structures such as electrodes or other conductive structures.

The metal can have a work function which is substantially the same as a native metal work function. For example, the difference can be 25% or less, or 10% or less.

Lines and grids can be formed. Multi-layer and multi-component metal features can be prepared.

SUBSTRATES

A wide variety of solid materials can be subjected to deposition of the metal inks. Polymers, plastics, metals, ceramics, glasses, silicon, semiconductors, and other solids can be used. Organic and inorganic substrates can be used. Polyester types of substrates can be used. Paper substrates can be used. Printed circuit boards can be used. Substrates used in applications described herein can be used.

Substrates can comprise electrodes and other structures including conductive or semiconductive structures.

APPLICATIONS

Deposition and patterning by direct-write methods, including inkjet printing, is described in, for example, Pique, Chrisey (Eds.), *Direct-Write Technologies for Rapid Prototyping Applications, Sensors, Electronics, and Integrated Power Sources*, Academic Press, 2002.

One application is forming semiconductor devices including transistors and field effect transistors. Transistors can comprise organic components including conjugated or conductive polymers.

Applications include electronics, printed electronics, flexible electronics, solar cells, displays, screens, light weight devices, LEDs, OLEDs, organic electronic devices, catalysis, fuel cells, RFID, and biomedical.

The deposited metal can be used as a seed layer for use with, for example, subsequent electroplating.

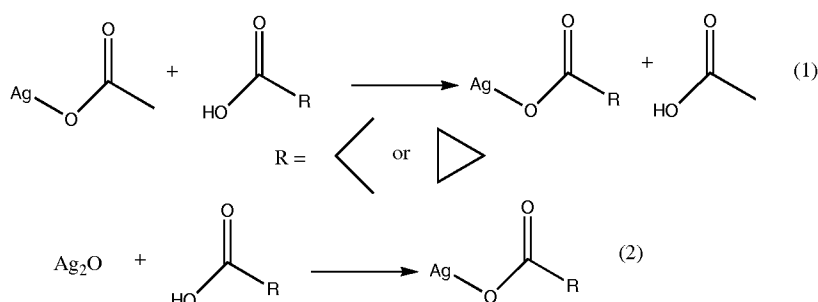
Other technology applications are described in, for example, "Flexible Electronics" by B.D. Gates, *Science*, vol 323, March 20, 2009, 1566-1567 including 2D and 3D applications.

Examples of patent literature describing methods and applications include, for example, US patent publications 2008/0305268; 2010/0163810; 2006/0130700; and US Patent Nos. 7,014,979; 7,629,017; 6,951,666; 6,818,783; 6,830,778; 6,036,889; 5,882,722.

WORKING EXAMPLES

Example 1. Silver Complexes

Precursors to both silver and gold complexes were silver carboxylates. For their synthesis, a known method based on Ag_2O (reaction 2) was compared to a cleaner, cheaper method based on silver acetate (reaction 1). These are shown below, and two exemplary R groups are shown. The Ag_2O method relies on a solid state reaction, failed to go to completion, and did not yield analytically pure materials. In contrast, the metathesis reaction between a carboxylic acid and silver acetate went to completion, afforded analytically pure compounds, and proceeded in quantitative yields. The elemental analysis of the two silver complexes from this reaction (1) were C, 24.59; H, 3.72 and C, 24.68; H, 2.56 for the isobutyrate and cyclopropate, respectively. Theoretical values are C, 24.64; H, 3.62 and C, 24.90; H, 2.61 for the isobutyrate and cyclopropate, respectively. Thus, approach (1) is superior to (2).

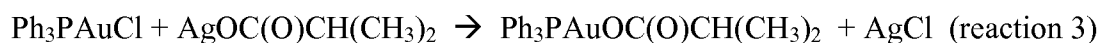


From the silver complexes, libraries of Ag-carboxylate amine compounds could be prepared that are viable for the production of metallic silver films, lines, and structures (vide infra).

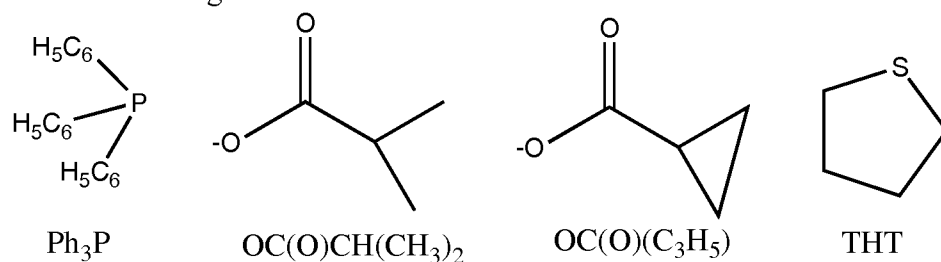
Example 2. Gold Complexes

The carboxylate compounds from Example 1 are also important intermediates in the production of R-Au-carboxylate complexes (gold inks) via the reaction of R-Au-Cl and Ag-carboxylate (R is a dative σ donor, or lone pair of electrons). The driving force in this reaction is the formation of a AgCl precipitate, whose low K_{sp} value and organic insolubility remove it from the reaction equilibrium making the overall yields quite high > 85%.

Examples of gold carboxylate complexes from the reaction of R-Au-Cl and Ag-carboxylate include:



Abbreviation legend and structures:



Initially, via this reaction as shown in reaction 3, known and unknown structures of triphenylphosphine gold carboxylate complexes were fabricated, and the crystal structure of one hitherto unknown species is shown in Figure 1. Although these showed excellent solubility in toluene and other aromatic hydrocarbons, they were not preferred to provide uniform films upon thermal treatment as they can result in well-separated gold nanoparticles with less pathway for conduction. This is possibly due to the presence of involatile triphenylphosphine in the starting precursor, which forms involatile triphenylphosphine oxide upon heating to yield an insulating matrix. The AFM (atomic force microscopy) image of these gold nanoparticles is shown in Figure 2.

Example 3. Other Gold Complexes including THT

Following the nanoparticle formation and results with the triphenylphosphine gold carboxylate complexes, a different perspective for the fabrication of Au films was developed. This approach was designed to, for example, (a) maximize metal content in the molecular precursor, (b) use ligands that were volatile while still being able to reduce the Au(I) to Au(0), (c) support the premise that the precursor complex remain soluble in aromatic hydrocarbon solvents, and/or (d) proceed in high overall yields.

Tetrahydrothiophene (THT) gold complexes were investigated. An entryway into this chemistry is, for example, through the reaction of commercially available HAuCl_4 and 2 equivalents of THT to yield known THT-Au-Cl. From this molecule, the reaction of a Ag-carboxylate with THT-Au-Cl can proceed with the formation of an insoluble AgCl by-product, that can be easily filtered off, yielding the desired, unknown THT-Au-carboxylates (reactions (4) and (5), preceeding page). Thus the THT molecule would reduce the Au(I), and the carboxylates would fissure to release CO_2 and a small organic radical that would abstract a hydrogen from a solvent.

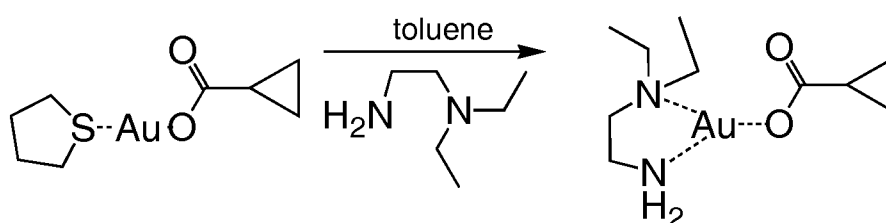
Shown in Figure 3 is the TGA (thermogravimetric analysis) of the gold complex (inset). On the y-axis is the percent mass loss and on the x-axis is temperature. Based on the theoretical value of approximately 53% gold residue for the proposed structure, one can see that the data is in good agreement with theory. This adds further credence that the postulated structure is indeed the composition of the product from the reaction of THT-Au-Cl and Ag-carboxylate. At this stage it is noteworthy that although the sharp transition begins at about 90°C , the THT-Au-carboxylate complexes slowly plate Au(0) at room temperature and can be stored cold, as neat oils or aromatic hydrocarbon solutions.

After the synthesis of the THT-Au-carboxylates, gold films were deposited using toluene precursor solutions (concentrations varied, but ranged up to 200 mg/mL) and Patch pipettes. As can be seen from the log resistivity versus temperature plots, complete metallization occurs at and before 110°C . Also, as the solutions age, the onset of metallization begins to decrease slightly in temperature. Alternatively, 100 mg/mL Au solutions have been spin-coated on UV/ozone cleaned glass and Si/SiO₂ at 1000-1300 rpm. The AFM images of the Au lines between two electrode pads show continuous metallization with excellent connectivity between the grains and low surface roughnesses. The SEM/EDXS measurements unequivocally show that Au is present and the line is coherent and continuous.

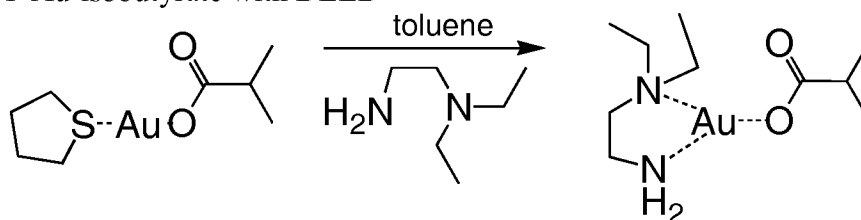
Example 4. Gold Amine Complexes including DEED

Because of the slight thermal instability and decreased longevity of the THT-Au-cyclopropate complex, and partly because silver amine complexes were performing very well, two gold complexes were reacted with N,N-diethylethylenediamine (DEED) (see below). The (THT)Au(carboxylates) were dissolved in toluene, and a large excess of DEED was added. The reaction was allowed to stir overnight, and the solution was filtered and placed under vacuum the next day. Both the cyclopropate and isobutyrate complexes were synthesized by analogous routes and their syntheses are shown below. Both exhibited increased metallization temperatures which suggests greater stability.

1) THT-Au-cyclopropate with DEED



THT-Au-isobutyrate with DEED



Example 5. Silver Amine Complexes including TMEDA and DEED

The new silver carboxylate compounds, synthesized from either Ag_2O or $\text{AgO}_2\text{C}_2\text{H}_3$ (silver acetate, a new method) *vide supra*, were reacted neat with different multidentate amines and tested for their viability as conducting ink materials. All reactions were done overnight at room temperature, the solutions were gravity filtered, and the excess amine removed in vacuo. Amine ligands can have ability to act as electron donating species (reductants) to achieve the transformation of Ag(I) to Ag(0) . Furthermore, they can afford volatile by-products that would minimize film impurities. The choice of carboxylate as the other ligand was to select chelators with a minimum number of atoms that would bear an anionic charge, making the molecule neutral and thus soluble in aromatic hydrocarbon solvents. It was envisioned that the carboxylate would again fissure to yield CO_2 (a gas) and volatile small organic molecules.

The reaction between silver cyclopropionate and N,N,N',N'-tetramethylethylenediamine (TMEDA) was attempted. Although successful, the product was a dinuclear silver complex with argentophilic interactions, intramolecular bridging carboxylates, and intermolecular bridging TMEDAs. After recrystallization from TMEDA, and despite the high metal content, the complex was found to be insoluble in toluene and hygroscopic.

1.) Synthesis of silver (I) cyclopropionate with N,N,N',N'-tetramethylethylenediamine (TMEDA)

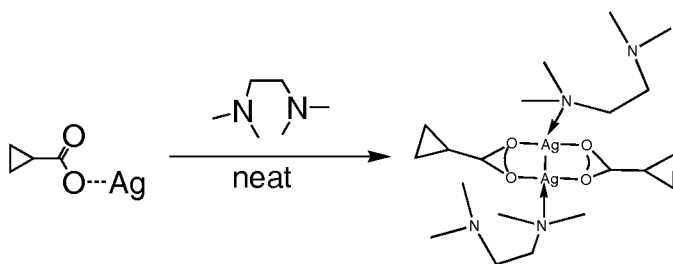


Figure 4 shows a diffraction-derived molecular structure of dinuclear complex from above reaction

Two drawbacks of the silver TMEDA system were solubility and moisture sensitivity. It was postulated that the solubility issue could be remedied by using an unsymmetrical, bidentate amine with longer alkyl chains on an N-terminus and a non-cyclic carboxylate, which could not pack effectively in the solid state. Concerning the latter, it was believed that the moisture sensitivity may be rooted in the weak argentophilic interaction (Ag-Ag bond) that would hydrolyze upon exposure to moisture under ambient conditions to place a H₂O molecule in the Ag coordination sphere. Thus, silver isobutyrate was used as one starting material and N,N-diethylethylenediamine (DEED) as the other reactant to hopefully yield more coordinately saturated, soluble, non-hygroscopic mononuclear molecules without Ag-Ag bonds.

2) Synthesis of silver (I) isobutyrate with N,N-diethylethylenediamine (DEED)

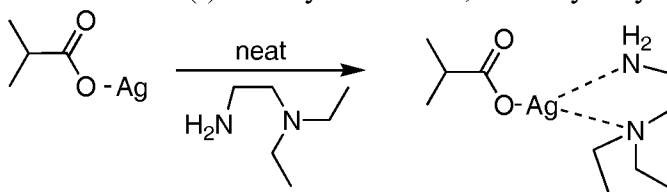


Figure 5 shows a diffraction-derived molecular structure of mononuclear complex from above reaction.

As can be seen from the single crystal x-ray structure (above), a mononuclear Ag(I) complex was synthesized containing a carboxylate and an unsymmetrical bidentate amine bearing N,N-diethyls. The coordination geometry about the silver ion is trigonal planar with both amine nitrogen bound and a single oxygen atom of the carboxylate coordinated. This complex is not moisture sensitive and is soluble in aromatic hydrocarbons such as toluene and xylenes. Thus, it provides a number of advantages.

Following the successful synthesis of the above compound, toluene solutions of 65-75 mg/mL concentrations were made, and lines were drawn between two gold electrode pads and annealed under ambient conditions. The change in resistivity was measured as a function of temperature, and the resulting metal was preliminarily characterized. Toward this goal the following data were obtained. Figure 6 is the change in log resistivity (y-axis) versus temperature (°C, x-axis). From this data, it is apparent that a striking loss (about 7 orders of magnitude) of resistivity occurs between 190 and 210°C. To test the composition and morphology of the resulting silver, scanning electron microscopy (SEM) and energy dispersive x-ray spectroscopy (EDXS) were performed. The former visualizes the material under high magnification, while the latter gives information about the elemental composition. The SEM image clearly shows silver metal adhering to the gold electrode. EDXS indicates that four elements are present Ag, Si, O, and C. The Si and O arise from the substrate and should not be considered, whereas the Ag and C are relevant. The carbon is most likely surface bound contamination. The resulting Ag(O) is metallic.

Figure 6 shows log resistivity versus temperature graph. Figure 7 shows SEM, and Figure 8 shows EDXS of the metallic silver deposited from the above Ag(I) complex. The EDXS data showed that only C, Si, O and Ag are present in the film, with Si and O originating from the substrate.

The solution deposition from a Patch pipette (above) was the initial method used to deposit the Ag ink. However this only served as a preliminary experiment prior to the inkjet deposition of silver lines using a 62.5mg/mL toluene ink. As can be seen in Figure 9, inkjet deposition was successful using a 30 μ m nozzle to afford approximately 200 μ m width lines.

Given the success of the (DEED)Ag(isobutyrate), carboxylates were changed and the cyclopropate anion as a coordinating ligand was explored.

It was initially somewhat surprising that this complex metallized at a slightly higher temperature than the analogous (DEED)Ag(isobutyrate). However, while the present inventions are not limited by scientific theory, the rationale may be uncovered by the crystalline packing of silver (I) cyclopropate with N,N,N',N'-tetramethylethylenediamine (TMEDA). In this structure, the cyclopropyl groups stack atop each other, stabilizing the molecular structure and similar behavior could be envisioned here. Following evaporation of the solvent, this molecule may align using the cyclopropyl groups as a zipper, thereby thermally stabilizing the resulting film yielding higher metallization temperatures.

Silver (I) cyclopropate with DEED

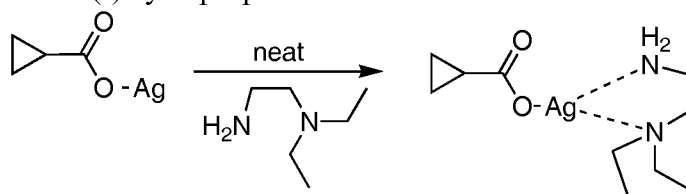
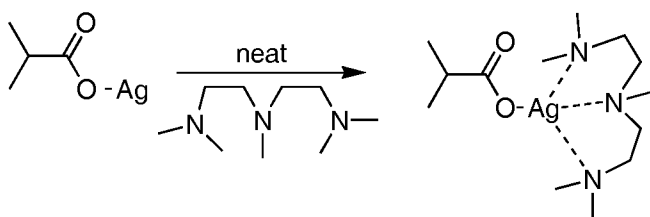


Figure 10 is the log resistivity versus temperature plot of a (DEED)Ag(cyclopropate) line drawn between two gold electrode pads on Si/SiO₂ from a 65 mg/mL toluene solution. As exhibited in this figure, one again sees an about 7 fold drop in resistivity over an approximately 50°C range starting at about 190°C. It is interesting that metallization occurs at a higher temperature, suggesting greater stability, which is what would be desirable in a product with significant shelf-life and longevity.

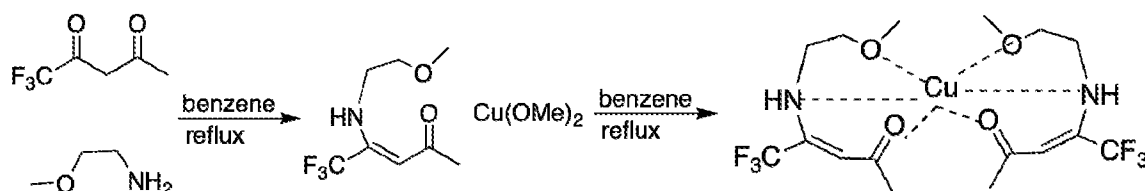
Concerning the silver, a tridentate amine (N,N,N',N',N''-pentamethyldiethylenetriamine (PMDETA), synthesis below) was employed as a coordinating ligand. As drawn, the tridentate amine is coordinated through all of its nitrogen donor atoms to yields a four coordinate complex. In Figure 11 is again a log resistivity versus temperature plot of a (PMDEA)Ag(isobutyrate) line drawn between two gold electrode pads on Si/SiO₂ from a 65mg/mL toluene solution. As can be seen this complex undergoes metallization at an even higher temperature than the previous two silver complexes with a nearly identical, 7 fold change in resistivity. This is most likely due to two factors. First, a four coordinate Ag(I) is less labile and mobile than a three coordinate cation, and second, the tridentate amine has a much higher boiling point than the bidentate amines making it less volatile and less apt to decompose to base metal.

- 1) Silver (I) cyclopropate with N,N,N',N',N''-pentamethyldiethylenetriamine (PMDETA)



Example 6. Copper Complex

A tridentate Schiff base ligand was synthesized by reaction of a partially fluorinated acetoacetone derivative with ethanolamine. The tridentate Schiff base was purified by recrystallization to yield about 50% product. This ligand was then reacted with copper methoxide, $\text{Cu}(\text{OMe})_2$ in benzene and refluxed overnight. A log resistivity versus temperature plot is also shown (Figure 12) indicating an approximate drop in resistivity of 4 orders of magnitude suggestive of the formation of copper metal. SEM/EDXS (Figures 13 and 14), between two gold electrode pads, confirms the presence of three elements, Cu, Si, and O. The Si and O both arrive from the substrate, whereas the copper comes from thermal decomposition of the complex.



Example 7. Additional Structural Information

Given the success of the $(\text{DEED})\text{Ag}(\text{isobutyrate})$, the cyclopropate anion was used as a coordinating ligand. As can be seen from the diffraction-derived molecular structure (Figure 15), this mononuclear complex contains the bidentate amine and the cyclopropyl carboxylate. The geometry about the four-coordinate Ag^{1+} ion is tetrahedral with both amine nitrogen atoms bound as well as both oxygen atoms from the carboxylate. In contrast, only one carboxylate oxygen was bonded in the aforementioned, previously shown, $(\text{DEED})\text{Ag}(\text{isobutyrate})$. The different thermal behavior (higher metallization temperatures) of this compound with two Ag-O interactions suggests that these (among packing factors, *vide infra*) may be responsible for the increased stability.

Example 8. Additional Embodiments including XPS and Work Function

Atomic Force Microscopy (AFM): An AFM image showed the presence of a Au(0) film deposited (spin cast, 1300 rpm from 100 mg/mL toluene solution) onto a glass substrate. As evidenced from this 25 μm^2 image, the height ranged from approximately 40 to 60 nm with a low rms surface roughness of 7.90 nm. The film was uniform without pinholes, defects, or nanoparticles and these observations were substantially continuous throughout the sampled areas. Following AFM measurements, the electrical properties of the sample were interrogated, and these are subsequently described (vide infra).

Electrical Conductivity Measurements: Electrical conductivity measurements were performed on thin films derived from (THT)Au-cyclopropate by the standard spring-loaded pressure-contact four-point probe method at ambient conditions. Films were formed from toluene solutions spun-cast at 1000-1300 rpm. Film metallization was then achieved by heating on a hotplate for about 1 minute to a temperature of about 150°C. This method led to Au films with thicknesses ranging from 20-50 nm. Conductivity was measured using a four-point probe station. Film thickness was measured by AFM on the punctures in the films made by the probes. Conductivity [$\text{S} \cdot \text{cm}^{-1}$] was calculated according to the following equation:

$$\sigma = \frac{1}{4.53 \times R \times l} \quad (1)$$

where R is the resistance ($R = V/I$) in Ω and l is the film thickness in cm. It was found that the Au formed from the spun-cast metal inks gave conductivities on the average of about $4 \times 10^6 \text{ S cm}^{-1}$, which is just one magnitude lower than what was observed with sputtered Au samples.

X-ray photoelectron spectroscopy (XPS) and Ultraviolet Photoelectron Spectroscopy (UPS): The interface was examined using XPS and UPS measurements.

Sample Preparation

The starting substrate was a highly doped (n+) Si wafer (1.5 X 1.5 inch²). The wafers were etched with buffered oxide etchant (BOE) in a class 100 clean-room at Carnegie Mellon University to remove the native oxide layer. Thereafter, the final samples were prepared as follows:

Sputtered Au film: 5 nm of Ti (adhesion layer) and 50 nm of Au were sputtered onto the doped n+ Si wafer.

Au thin film from metal precursor solution: The n+ Si wafer was cleaned at 120°C in an UV-O₃ plasma cleaner for 20 minutes. The wafer was then placed on a hot plate initially at room

temperature. Thereafter the Au precursor solution was dropped onto the wafer as a 100 mg/mL toluene solution. The temperature was then increased to $\sim 150\text{ }^{\circ}\text{C}$ to evaporate the solvent and form the metal film.

XPS and UPS measurements

The measurements were conducted using a scanning multiprobe surface analysis system-Phi 5000 Versaprobe. This system comprises a monochromatic focused Al K α X-ray (1486.7 eV) source, a He source and a hemispherical analyzer.

XPS settings: The X-ray beam was incident normal to the sample unless specified, and the emitted photoelectrons were collected at an emission angle of 45° relative to the sample normal. Wide scan data were collected using pass energy of 117.4 eV. High-resolution scans were obtained using pass energy of 23.5 eV. The XPS spectra were referenced to an energy scale with binding energies for Cu 2p $_{3/2}$ at $932.67 \pm 0.05\text{ eV}$ and Au 4f at $84.0 \pm 0.05\text{ eV}$. The sputter cleaning of the samples were carried out using 2 kV Ar $^{+}$ sputtering over a 3 mm $\times$ 3 mm area of the specimen. The sputter rate for 2 kV Ar $^{+}$ over a 3 mm X 3 mm raster area is determined to be 6.5 nm/min, using SiO $_2$ /Si reference material with known thickness from X-ray reflectivity and ellipsometry.

UPS settings: UPS measurements were conducted using the He I ($h\nu=21.2\text{ eV}$) line. The pass-energy used was 0.585 eV. During UPS measurements -5 V bias was applied to the sample in order to separate sample and analyzer high binding energy cutoffs.

The XPS and UPS spectra were processed using the CasaXPS software licensed by PNNL (Pacific Northwest National Laboratory). Work function values were determined from the UPS spectra by linear fit of the high and low binding energy cutoffs (secondary cut-off edge and Fermi-edge respectively) of the spectra and determination of their intersections with the binding energy axis.

XPS Results

XPS is a surface science technique whose penetration depth (the sampling depth from the vacuum level at the sample top) is about 50 to 65 Å. It is capable of exploring the atomic compositions of thin films as well as their neighboring atoms, oxidation states, and relative

abundance. For each and every element, there will be a characteristic binding energy associated with each core atomic orbital i.e. each element will give rise to a characteristic set of peaks in the x-ray photoelectron spectrum at kinetic energies determined by the photon energy and the respective binding energies.

The presence of peaks at particular energies therefore indicates the presence of a specific element in the sample under study - furthermore, the intensity of the peaks is related to the concentration of the element within the sampled region. Thus, the technique provides a quantitative analysis of the surface composition.

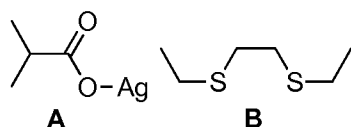
In gold films deposited from solution, 100 mg/mL toluene solutions drop cast on a n-doped Si square and heated to about 150°C, four elements are observed – Au, Ag, C, and O. The adventitious Ag is an expected result of the Au precursor synthesis (vide supra) and can be removed by further filtering of the precursor solution or centrifugation of the reaction followed again by filtering. However, in this sample its presence was constant throughout the film. The C and O can result from either surface contamination (commonly seen in XPS from handling the sample under ambient conditions before load-locking into the ultrahigh vacuum chamber) or from incomplete thermal decomposition of the precursor solution. Via sputtering experiments, these light elements most likely originate from the former method of contamination. As can be seen (Figure 16) from depth profiling XPS spectra (sputtered with Ar^+ which slowly ablates the surface, hence the term “depth profiling”) the Au and Ag peaks remain constant (the Au actually increases as the C and O are removed by the impinging Ar^+ ions) whereas the C and O peaks significantly decrease or disappear, respectively. The elemental compositions of a film sputtered for four minutes (in our hands the maximum time for which the experiments were undertaken) are as follows: Au (70.3%), Ag (5.8%), C (17.9%), and O (5.9%). The binding energy position of the Au 4f peak unequivocally shows that gold is in the zero oxidation state and as such can be considered metallic (further confirmed by UPS). Based on the peak positions of the C and O atoms, these are most likely bonded to each other and most likely exist as either carbonates or carboxylates, again resulting from either spurious atmospheric contamination or incomplete combustion of the precursors in air.

An important piece of data is the UPS spectrum (Figure 17). UPS is an extremely surface sensitive technique that explores the outermost 1-2 unit cells (10 Å) of sample. From this spectrum, one can determine that the Au film is indeed metallic and behaves as a metal with respect to incoming photons. It also allows one to calculate the gold work function (ϕ_{Au})

based on differences between the Fermi level energy (E_F) and the cut-off energy (E_{CO}). Based on this calculation, ϕ_{Au} was determined from the film derived from a precursor solution to be 4.9 eV. For a sputtered gold sample, our standard comparison, the ϕ_{Au} is 4.7 eV. This means that the gold system described herein is compatible with the semiconducting organic polymers using to fabricate thin film transistors.

Example 9. Additional Embodiments, Structural Information, Silver Thioether

It has been theorized that sulfur compounds can act as a better reductant when compared to nitrogen. As such, a sulfur-compound with enough side chains to ensure solubility was sought. A commercially available compound, 3,6-dithiaoctane was found, with the synthesis also readily available in literature. As such the dithioether (**B**) is not a new compound. Silver isobutyrate, described in a previous section, was reacted with 3,6-dithiaoctane in toluene and refluxed overnight. The solution was then filtered and the solvent was removed with vacuum. The remaining yellow solid was then examined for its chemical composition and its ability to form Ag(0) metal.



Crystals were grown, sent for analysis and the diffraction-derived structure was obtained shown in Figure 18. Notice the argentophilic interactions (i.e., dimerization of the silver centers) as well as the intermolecular bridging sulfur ligands. This structure may be quite similar to the initial silver TMEDA complex previously communicated. However, this silver thioether complex is quite soluble in aromatic organic solvents. Using a 100 mg/mL toluene solution of the metal complex and a Patch pipette, lines were drawn between two gold electrode pads, annealed under ambient conditions, and a preliminary analysis of thermal stability was measured. Looking at the change in resistivity as a function of temperature (Figure 19), it can be seen that the silver thioether complex decomposes into base metal at about 100°C, which is a *much lower* temperature when compared to all of the silver amine complexes (> 100°C). This lower metallization temperature is attributed to the stronger reducing power of the thioether compared to amine ligands.

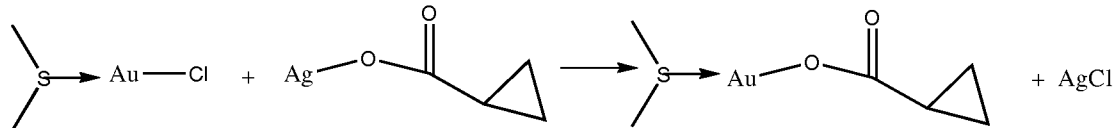
Figure 19 shows Log resistivity vs. temperature graph, and Figure 20 shows drawn silver line between gold electrodes after metallization.

The metal complex was also quite stable, both in solution and in crystalline form. As a solid, it can be stored in a refrigerator for weeks, perhaps or most likely indefinitely, with seemingly no or little change in its appearance or properties. In solution, it recrystallized after some time, but can be readily re-dissolved in a warm water bath and used again.

In summary, the synthesis and characterization of a new silver thioether complex is shown, its crystal structure presented, and it was used to deposit silver metal. The use of sulfur containing ligands represents a departure from our previous efforts on nitrogenous ligands, and because of its superior reducing power affords lower metallization temperatures.

Example 10. Dimethylthioether

Although the THT-Au-carboxylate complexes showed promising metalizations results leading to metallic gold at low temperatures (90 - 100°C) their thermal stability was slightly less than desirable as they had to be stored at -35°C, at which temperature they are indefinitely stable. This may be the result of the low steric encumbrances afforded by the THT ligand, whose methylene groups alpha to the sulfur atom were pinned back by an ethane bridge. To address this shortcoming, it was sought to increase the thioether sterics about the



gold ion by using a dimethylthioether (or dimethyl sulfide) ligand. This also removes two carbon and four hydrogen atoms compared to the THT ligand thereby increasing the metal content available for metallization. The synthesis is shown above. The reaction was performed with overnight stirring at room temperature in toluene using commercially available $\text{C}_2\text{H}_6\text{SAuCl}$. Its driving force is formation of the insoluble AgCl precipitate that is removed by simple gravity filtration. This rationale proved to be correct, as the increased steric bulk about the Au atom imparts greater stability and this complex is indefinitely stable at 0°C. Surprisingly it metalizes at a similar temperature as the THT-Au-carboxylates and affords high quality gold films with exceptional conductivities.

This complex crystallized from toluene solutions, and a suitable crystal for x-ray diffraction was identified. The diffraction-derived molecular structure exhibits 3 independent Au atoms with both terminal and bridging sulfurs as well as singly bound carboxylates. There are formal aurophilic interactions between the gold atoms. The derived molecular structure is shown in Figure 29.

Example 11. Additional Examples.

Figure 21 illustrates additional aspects for the synthesis of metal complexes. The only required purification step is a simple filtration. The reactions proceed in high yield and analytical purity. The compounds are stable toward air and moisture. The final product should be stored cold to reduce gold formation.

Figure 22 shows a microcapillary approach controlled initially by a micromanipulator arm, and then a final approach by piezo stack.

Figure 23 shows impact of aging on resistivity versus temperature plots.

Figure 24 shows a drawn gold line and gold pads.

Figure 25 shows EDX data showing high content of gold.

Figure 26 shows an experiment for ink jet printing of gold line, with 10 mg THTAuCyclopropanate/1 mL dry xylenes solution, 5 mm/sec travel time, 1 drop/0.04 mm, with 30 micron printhead aperture on SiO₂.

Figure 27 shows XPS of gold peaks comparing precursor solution approach versus sputtering approach.

Figure 28 provides additional conductivity and resistivity data, as well as an AFM image, for a gold film.

66 EMBODIMENTS DESCRIBED IN US PROVISIONAL APPLICATION 61/259,614

The following 66 embodiments are described in US provisional application 61/259,614 which are incorporated by reference in their entirety.

Embodiment 1. A composition comprising at least one metal complex comprising at least one metal and at least two ligands, wherein at least one first ligand is a sigma donor to the metal and volatilizes upon heating the metal complex, and at least one second ligand different from the first which also volatilizes upon heating the metal complex, wherein the metal complex is soluble in a solvent at 25°C.

Embodiment 2. The composition of embodiment 1, wherein the metal is silver, gold, copper, or platinum.

Embodiment 3. The composition of embodiment 1, wherein the metal is silver, gold, or copper.

Embodiment 4. The composition of embodiment 1, wherein the metal is silver or gold.

Embodiment 5. The composition of embodiment 1, wherein the metal complex comprises only one metal center.

Embodiment 6. The composition of embodiment 1, wherein the metal is in an oxidation state of (I) or (II).

Embodiment 7. The composition of embodiment 1, wherein the first ligand is a bidentate ligand.

Embodiment 8. The composition of embodiment 1, wherein the first ligand is a tridentate ligand.

Embodiment 9. The composition of embodiment 1, wherein the first ligand is an amine compound comprising at least two nitrogen.

Embodiment 10. The composition of embodiment 1, wherein the first ligand is an unsymmetrical amine compound comprising at least two nitrogen.

Embodiment 11. The composition of embodiment 1, wherein the first ligand is a thiophene or an amine. The thiophene can be tetrahydrothiophene.

Embodiment 12. The composition of embodiment 1, wherein the first ligand is not a phosphine.

Embodiment 13. The composition of embodiment 1, wherein the second ligand is a carboxylate.

Embodiment 14. The composition of embodiment 1, wherein the second ligand is a carboxylate comprising an alkyl group.

Embodiment 15. The composition of embodiment 1, wherein the second ligand is a carboxylate represented by -OOC-R , wherein R is an alkyl group, wherein R has 10 or fewer carbon atoms.

Embodiment 16. The composition of embodiment 1, wherein the second ligand is a carboxylate represented by OOC-R , wherein R is an alkyl group, wherein R has 5 or fewer carbon atoms.

Embodiment 17. The composition of embodiment 1, wherein the composition is substantially free of nanoparticles.

Embodiment 18. The composition of embodiment 1, wherein the composition is totally free of nanoparticles.

Embodiment 19. The composition of embodiment 1, wherein the composition has a sharp decomposition transition beginning at a temperature of less than 200°C .

Embodiment 20. The composition of embodiment 1, wherein the composition has a sharp decomposition transition beginning at a temperature of less than 150°C .

Embodiment 21. The composition of embodiment 1, wherein the composition can be stored at about 25°C for at least 100 hours without substantial deposition of metal (0).

Embodiment 22. The composition of embodiment 1, wherein the composition further comprises at least one solvent for the complex.

Embodiment 23. The composition of embodiment 1, wherein the composition further comprises at least one aromatic hydrocarbon solvent.

Embodiment 24. The composition of embodiment 1, wherein the composition further comprises at least one solvent, and the concentration of the complex is about 200 mg/mL or less.

Embodiment 25. The composition of embodiment 1, wherein the solvent is an aromatic hydrocarbon solvent.

Embodiment 26. The composition of embodiment 1, wherein the metal complex comprises at least 25 wt.% metal.

Embodiment 27. The composition of embodiment 1, wherein the metal complex comprises at least 50 wt.% metal.

Embodiment 28. The composition of embodiment 1, wherein the metal complex comprises at least 70 wt.% metal.

Embodiment 29. The composition of embodiment 1, wherein the second ligand is a carboxylate, and the first ligand is a polydentate amine, and the metal is silver, gold, or copper.

Embodiment 30. The composition of embodiment 1, wherein the second ligand is a carboxylate, the first ligand is a polydentate unsymmetrical amine, the metal is silver or gold, and wherein the solvent is toluene.

Embodiment 31. A composition comprising a complex comprising a coinage metal, a carboxylate ligand, and tetrahydrothiophene ligand.

Embodiment 32. A composition comprising a tetrahydrothiophene gold carboxylate complex.

Embodiment 33. A composition comprising a tetrahydrothiophene gold isobutyrate complex.

Embodiment 34. A composition comprising a tetrahydrothiophene gold cyclopropate complex.

Embodiment 35. A composition comprising a tetrahydrothiophene gold complex, wherein said complex is transformed into metallic gold and volatile non-metallic material

upon heating above about 90°C.

Embodiment 36. A composition comprising a complex comprising a coinage metal, a carboxylate ligand, and an unsymmetrical bidentate amine, said amine bearing N,N-diethyls.

Embodiment 37. A composition comprising a N,N-diethylethylenediamine gold carboxylate complex.

Embodiment 38. A composition comprising a N,N-diethylethylenediamine gold isobutyrate complex.

Embodiment 39. A composition comprising gold complexed with carboxylate and amine.

Embodiment 40. A composition comprising a N,N-diethylethylenediamine gold cyclopropate complex.

Embodiment 41. A composition comprising a N,N-diethylethylenediamine gold complex, wherein said complex is transformed into metallic gold and volatile non-metallic material upon heating above about 90°C.

Embodiment 42. A composition comprising a N,N-diethylethylenediamine silver carboxylate complex.

Embodiment 43. A composition comprising a N,N-diethylethylenediamine silver isobutyrate complex.

Embodiment 44. A composition comprising a N,N-diethylethylenediamine silver isopropate complex.

Embodiment 45. A composition comprising a N,N-diethylethylenediamine silver complex, wherein said complex is transformed into metallic silver and volatile non-metallic material upon heating above about 190 °C.

Embodiment 46. A composition comprising a complex comprising a coinage metal, a carboxylate, and a tridentate amine, said amine bearing N,N,N',N',N''-pentamethyls.

Embodiment 47. A composition comprising a N,N,N',N',N''-pentamethyldiethylenetriamine silver carboxylate complex.

Embodiment 48. A composition comprising a N,N,N',N',N''-pentamethyldiethylenetriamine silver isobutyrate complex.

Embodiment 49. A composition comprising a N,N,N',N',N''-pentamethyldiethylenetriamine silver complex, wherein said complex is transformed into metallic silver and volatile non-metallic material upon heating above about 90°C.

Embodiment 50. A composition comprising a coinage metal and a tridentate Schiff base ligand.

Embodiment 51. A composition comprising copper and a tridentate Schiff base ligand.

Embodiment 52. A composition comprising
 $\text{Cu}(\text{NH}(\text{CH}_2\text{CH}_2\text{OCH}_3)(\text{C}(\text{CF}_3)\text{CHCOCH}_3))$.

Embodiment 53. A composition comprising a complex comprising copper and a tridentate Schiff base ligand, wherein said complex is transformed into metallic copper and volatile non-metallic material upon heating above about 90°C.

Embodiment 54. An ink comprising a composition according to embodiments 31-53, optionally further comprising solvent.

Embodiment 55. A method comprising: depositing an ink on a surface, wherein the ink comprises a composition according to embodiments 1-54, and producing a conductive metal film by heating or irradiating said ink.

Embodiment 56. The method of embodiment 55, wherein the depositing is carried out by inkjet deposition.

Embodiment 57. The method of embodiment 55, wherein the producing is carried out by heating at a temperature of about 250°C or less.

Embodiment 58. An article comprising a conductive metal film produced according to the methods of embodiments 55-57.

Embodiment 59. A method comprising: reacting tetrahydrothiophene gold chloride with a silver carboxylate to produce a tetrahydrothiophene gold carboxylate and silver chloride.

Embodiment 60. A method comprising: reacting a tetrahydrothiophene gold carboxylate with a diamine to produce a diamine gold carboxylate complex.

Embodiment 61. A method comprising: reacting a silver carboxylate with an unsymmetrical bidentate amine to produce an amine silver carboxylate complex.

Embodiment 62. A method comprising: reacting a silver carboxylate with a tridentate amine to produce an amine silver carboxylate complex.

Embodiment 63. A method comprising: reacting a copper methoxide with a tridentate Schiff base to produce a complex comprising copper and said tridentate Schiff base.

Embodiment 64. A composition comprising a complex produced according to the methods of embodiments 59-63.

Embodiment 65. A composition comprising at least one metal complex comprising at least one metal and at least two ligands, wherein at least one first ligand is an amino ligand, and at least one second ligand different from the first which is a carboxylate, wherein the metal complex is soluble in a solvent at 25°C, and wherein the content of metal in the complex is at least 50 wt.%.

Embodiment 66. A composition comprising at least one neutral metal complex comprising at least one metal in a (I) or (II) oxidation state, and at least two ligands, wherein at least one first ligand is a neutral sigma donor to the metal and volatilizes upon heating the metal complex to a temperature below 150°C, and at least one second anionic ligand different from the first which also volatilizes upon heating the metal complex to a temperature below 150°C, wherein the metal complex is soluble in a solvent at 25°C.

WHAT IS CLAIMED IS:

1. A composition comprising at least one metal complex comprising at least one metal and at least two ligands, wherein at least one first ligand is a sigma donor to the metal and volatilizes upon heating the metal complex, and at least one second ligand different from the first which also volatilizes upon heating the metal complex, wherein the metal complex is soluble in a solvent at 25°C.
2. The composition of claim 1, wherein the metal is silver, gold, copper, platinum, or ruthenium.
3. The composition of claim 1, wherein the metal complex comprises only one metal center.
4. The composition of claim 1, wherein the metal is in an oxidation state of (I) or (II).
5. The composition of claim 1, wherein the first ligand is a monodentate ligand.
6. The composition of claim 1, wherein the first ligand is a bidentate ligand.
7. The composition of claim 1, wherein the first ligand is a tridentate ligand.
8. The composition of claim 1, wherein the first ligand is an amine compound comprising at least two nitrogen.
9. The composition of claim 1, wherein the first ligand is an unsymmetrical amine compound comprising at least two nitrogen.
10. The composition of claim 1, wherein the first ligand is an amine.
11. The composition of claim 1, wherein the first ligand is a sulfur-containing ligand.
12. The composition of claim 1, wherein the first ligand is a thioether.

13. The composition of claim 1, wherein the first ligand is not a phosphine.
14. The composition of claim 1, wherein the second ligand is a carboxylate.
15. The composition of claim 1, wherein the second ligand is a carboxylate comprising an alkyl group.
16. The composition of claim 1, wherein the second ligand is a carboxylate represented by OOC-R, wherein R is an alkyl group, wherein R has 5 or fewer carbon atoms.
17. The composition of claim 1, wherein the composition is substantially free of nanoparticles.
18. The composition of claim 1, wherein the composition is totally free of nanoparticles.
19. The composition of claim 1, wherein the composition has a sharp decomposition transition beginning at a temperature of less than 200°C.
20. The composition of claim 1, wherein the composition has a sharp decomposition transition beginning at a temperature of less than 150°C.
21. The composition of claim 1, wherein the composition can be stored at about 25°C for at least 100 hours without substantial deposition of metal (0).
22. The composition of claim 1, wherein the composition further comprises at least one solvent for the complex.
23. The composition of claim 1, wherein the composition further comprises at least one aromatic hydrocarbon solvent.
24. The composition of claim 1, wherein the composition further comprises at least one solvent, and the concentration of the complex is about 200 mg/mL or less.
25. The composition of claim 1, wherein the solvent is an aromatic hydrocarbon solvent.

26. The composition of claim 1, wherein the metal complex comprises at least 25 wt.% metal.
27. The composition of claim 1, wherein the metal complex comprises at least 50 wt.% metal.
28. The composition of claim 1, wherein the metal complex comprises at least 70 wt.% metal.
29. The composition of claim 1, wherein the second ligand is a carboxylate, and the first ligand is a polydentate amine, and the metal is silver, gold, or copper.
30. The composition of claim 1, wherein the second ligand is a carboxylate, the first ligand is a polydentate unsymmetrical amine, the metal is silver or gold, and wherein the solvent is toluene or a xylene.
31. A composition comprising at least one metal complex comprising at least one metal and at least two ligands, wherein at least one first ligand is a sulfur-containing ligand, and at least one second ligand different from the first which, optionally, is a carboxylate, wherein the metal complex is soluble in a solvent at 25°C.
32. The composition of claim 31, wherein the content of metal in the complex is at least 50 wt.%, and the composition is substantially free of nanoparticles.
33. The composition of claim 31, wherein the sulfur-containing ligand is a cyclic or linear thioether ligand.
34. The composition of claim 31, wherein the sulfur containing ligand is a cyclic thioether.
35. The composition of claim 31, wherein the sulfur-containing ligand is a dialkylthioether.
36. The composition of claim 31, wherein the sulfur-containing ligand is a dithiaalkane.

37. The composition of claim 31, wherein the sulfur-containing ligand is a dithiooctane.
38. The composition of claim 31, wherein the sulfur-containing ligand comprises one or two sulfur atoms.
39. The composition of claim 31, wherein the sulfur-containing ligand is a bidentate ligand.
40. The composition of claim 31, wherein the sulfur-containing ligand has six carbons or less.
41. A composition comprising at least one metal complex comprising at least one metal and at least two ligands, wherein at least one first ligand is an amino ligand, and at least one second ligand different from the first which, optionally, is a carboxylate, wherein the metal complex is soluble in a solvent at 25°C.
42. The composition of claim 41, wherein the content of metal in the complex is at least 50 wt.%, and the composition is substantially free of nanoparticles.
43. The composition of claim 41, wherein the second ligand is a carboxylate.
44. The composition of claim 41, wherein the metal is silver, gold, copper, platinum, or ruthenium.
45. The composition of claim 41, wherein the metal complex comprises only one metal center.
46. The composition of claim 41, wherein the metal is in an oxidation state of (I) or (II).
47. The composition of claim 41, wherein the first ligand is a monodentate ligand.
48. The composition of claim 41, wherein the first ligand is a bidentate ligand.
49. The composition of claim 41, wherein the first ligand is a tridentate ligand.

50. The composition of claim 41, wherein the first ligand is an unsymmetrical amino ligand comprising at least two nitrogen.
51. A composition comprising at least one neutral metal complex comprising at least one metal in a (I) or (II) oxidation state, and at least two ligands, wherein at least one first ligand is a neutral sigma donor to the metal and volatilizes upon heating the metal complex to a temperature below 150°C, and at least one second anionic ligand different from the first which also volatilizes upon heating the metal complex to a temperature below 150°C, wherein, optionally, the metal complex is soluble in a solvent at 25°C.
52. The composition of claim 51, wherein the first ligand is a sulfur-containing ligand.
53. The composition of claim 51, wherein the first ligand is tetrahydrothiophene.
54. The composition of claim 51, wherein the first ligand is a thioether.
55. The composition of claim 51, wherein the first ligand comprises at least two sulfurs.
56. The composition of claim 51, wherein the first ligand has six or fewer carbon atoms.
57. The composition of claim 51, wherein the first ligand has four or fewer carbon atoms.
58. The composition of claim 51, wherein the first ligand has two or fewer carbon atoms.
59. The composition of claim 51, wherein the first ligand second ligand is a carboxylate.
60. The composition of claim 51, wherein the number of carbon atoms in the complex is twelve or less.
61. A method comprising:
 depositing an ink on a surface, wherein the ink comprises a composition according to claims 1-60, and
 producing a conductive metal film by heating or irradiating said ink.

62. The method of claim 61, wherein the producing step is carried out by heating.
63. The method of claim 61, wherein the producing step is carried out by irradiating.
64. The method of claim 61, wherein the ink comprises a composition according to claim 1.
65. The method of claim 61, wherein the ink comprises a composition according to claim 31.
66. The method of claim 61, wherein the ink comprises a composition according to claim 41.
67. The method of claim 61, wherein the ink comprises a composition according to claim 51.
68. The method of claim 61, wherein the metal is gold, silver, or copper.
69. The method of claim 61, wherein the ink is substantially free of nanoparticles before deposition.
70. The method of claim 61, wherein the ink is substantially free of nanoparticles after deposition.
71. The method of claim 61, wherein the depositing is carried out by inkjet deposition.
72. The method of claim 61, wherein the producing is carried out by heating at a temperature of about 250°C or less.
73. The method of claim 61, wherein the producing is carried out by heating at a temperature of about 200°C or less.
74. The method of claim 61, wherein the producing is carried out by heating at a temperature of about 150°C or less.
75. The method of claim 61, wherein the film is in the form of a line, and the line has a conductivity of at least 1,000 S/cm.

76. The method of claim 61, wherein the film is in the form of a line, and the line has a conductivity of at least 5,000 S/cm.
77. The method of claim 61, wherein the film is in the form of a line, and the line has a conductivity of at least 10,000 S/cm.
78. The method of claim 61, wherein the film is in the form of a line, and the line has a work function which is within 25 percent of the work function of the pure metal.
79. The method of claim 61, wherein the film is in the form of a line, and the line has a work function which is within 10 percent of the work function of the pure metal.
80. The method of claim 61, wherein the film is in the form of a line, and the line has a work function which is within 5 percent of the work function of the pure metal.
81. A method comprising:
 depositing an ink on a surface to form a deposit, converting the deposit to a metal film, wherein the metal film shows a work function which is within 25 percent of the work function of the pure metal.
82. The method of claim 81, wherein the deposit is heated.
83. The method of claim 81, wherein the deposit is irradiated.
84. The method of claim 81, wherein the ink comprises a composition according to claims 1-60.
85. The method of claim 81, wherein the ink comprises a composition according to claim 1.
86. The method of claim 81, wherein the ink comprises a composition according to claim 31.
87. The method of claim 81, wherein the ink comprises a composition according to claim 41.
88. The method of claim 81, wherein the ink comprises a composition according to claim 51.

89. The method of claim 81, wherein the metal is gold, silver, or copper.
90. The method of claim 81, wherein the ink is substantially free of nanoparticles before deposition.
91. The method of claim 81, wherein the ink is substantially free of nanoparticles after deposition.
92. The method of claim 81, wherein the depositing is carried out by inkjet deposition.
93. The method of claim 81, wherein the converting is carried out by heating at a temperature of about 250°C or less.
94. The method of claim 81, wherein the converting is carried out by heating at a temperature of about 200°C or less.
95. The method of claim 81, wherein the converting is carried out by heating at a temperature of about 150°C or less.
96. The method of claim 81, wherein the film is in the form of a line, and the line has a conductivity of at least 1,000 S/cm.
97. The method of claim 81, wherein the film is in the form of a line, and the line has a conductivity of at least 5,000 S/cm.
98. The method of claim 81, wherein the film is in the form of a line, and the line has a conductivity of at least 10,000 S/cm.
99. The method of claim 81, wherein the film is in the form of a line, wherein the metal film shows a work function which is within 10 percent of the work function of the pure metal.
100. The method of claim 81, wherein the film is in the form of a line, wherein the metal film shows a work function which is within 5 percent of the work function of the pure metal.

101. A composition comprising at least one metal complex comprising at least one metal and at least two ligands, wherein at least one first ligand is a sigma donor to the metal and volatilizes upon heating the metal complex, and at least one second ligand which also volatilizes upon heating the metal complex, wherein the metal complex is soluble in a solvent at 25°C.

102. The composition of claim 101, wherein the first ligand and the second ligand are the same ligand.

103. The composition of claim 101, wherein the first ligand and the second ligand are different ligands.

104. The composition of claim 101, wherein the metal is copper.

105. The composition of claim 101, wherein the first ligand comprises at least one nitrogen atom and at least two oxygen atoms.

106. The composition of claim 101, wherein the first ligand and the second ligand are the same ligand, and wherein the first ligand comprises at least one nitrogen atom and at least two oxygen atoms.

107. The composition of claim 101, wherein the first ligand and the second ligand are the same ligand, and wherein the first ligand comprises at least one nitrogen atom and at least two oxygen atoms, as well as at least one fluorine.

108. The composition of claim 101, wherein the first ligand is a tridentate ligand.

109. The composition of claim 101, wherein the first ligand is a tridentate Schiff base ligand.

110. The composition of claim 101, wherein the first ligand comprises at least one secondary amine group, at least one carbonyl group, and at least one ether group.

111. A composition comprising at least one metal complex comprising at least one metal and at least two ligands, wherein at least one first ligand is a sigma donor to the metal and volatilizes upon heating the metal complex to a temperature of about 250°C or less, and at least one second ligand, which is optionally different from the first, which also volatilizes upon heating the metal complex to a temperature of about 250°C or less.

112. The composition of claim 111, wherein the metal complex is heated to a temperature of 150°C or less.

113. The composition of claim 111, wherein the metal complex is soluble at 25°C.

114. The composition of claim 111, wherein the composition upon heating provides a metal with a work function which is within 25 percent of the work function of the pure metal.

115. The composition of claim 111, wherein the composition upon heating provides a metal composition having a conductivity of at least 1,000 S/cm.

116. A method comprising:

depositing an ink on a surface to form a deposit, converting the deposit to a metal film, wherein the metal film shows a conductivity of at least 1,000 S/cm.

117. The method of claim 116, wherein the conductivity is at least 5,000 S/cm.

118. The method of claim 116, wherein the conductivity is at least 10,000 S/cm.

119. The method of claim 116, wherein the converting is carried out by heating at a temperature of about 200°C or less.

120. The method of claim 116, wherein the converting is carried out by heating at a temperature of about 150°C or less.

121. A composition comprising at least one metal complex consisting essentially of at least one metal and at least two ligands bonded to the metal, wherein at least one first ligand is a neutral donor to the metal and volatilizes upon heating the metal complex, and at least one

second ligand different from the first which also volatilizes upon heating the metal complex and is negatively charged.

122. The composition of claim 121, wherein the first ligand consists essentially of nitrogen and/or sulfur.

123. The composition of claim 121, wherein the second ligand consists essentially of a carboxylate.

124. The composition of claim 121, wherein the complex is soluble in toluene.

125. The composition of claim 121, wherein the complex consisting essentially of the metal, the first ligand, and the second ligand is neutrally charged.