

METHOD OF FABRICATING PATTERNS AND OBJECTS

TECHNOLOGICAL FIELD

The present disclosure generally relates to indirect methods for fabricating structures on a substrate.

BACKGROUND

Direct deposition of thin metal films and metallic patterns on surfaces at low temperatures, particularly on insulating materials, is a major challenge. The demand for this kind of technology is driven by industries interested in developing metallic interconnections for electronics at low cost. One of the most promising R&D directions involves fabrication of flexible electronic devices by printing, otherwise known as printed electronics [1].

One of the essential technologies for printed electronics is the printing of conductive interconnections for various electronic and optoelectronic devices. The main challenge in this growing research area is to fabricate these connections at low cost, by simple processes, including those suitable for plastic substrates.

There are several known techniques for printing patterns of conductor materials, particularly metals, CNTs, graphene and conductive polymers, onto various surfaces. These include subtractive processes like photolithography and additive processes that include directed chemical fabrication, such as electroless deposition of metals and graphene. Additive methods also include well-established printing processes such as transfer gravure, inkjet, screen and flexo [2-4]. Transfer printing may involve contact processes like stamping or non-contact processes, where the printed material is transferred from a donor to an acceptor substrate positioned in its vicinity through the gas phase. For example, a transfer technique is sublimation printing used in the textile industry [5-6].

Sputter deposition is a method for depositing thin films that involves eroding material from a "target" source onto a "substrate", e.g., a silicon wafer under vacuum conditions. Sputtered atoms ejected into the gas phase are not in their thermodynamic equilibrium state, and tend to deposit on all surfaces in the vacuum chamber. A substrate (such as a wafer) placed in the chamber will be coated with a thin film without

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a defined pattern. Sputtering usually uses argon plasma and requires high cost equipment. In order to prepare a pattern, a special mask is used to block the sputtered material from non-patterned areas; this adds to the complexity and cost of the process.

Another way to achieve a pattern is through chemical etching of a copper film by using complicated photolithography processes, which also requires a mask. The problems associated with electroless deposition are that it requires several steps, including wet chemistry and the printed catalysts are expensive metals (e.g., Pd).

Currently there is a need for a method to pattern conductive structures by direct printing. Most printing technologies require a liquid ink for printing conductors; such are based on two main approaches: The first approach is by use of an ink that contains metallic nanoparticles (NPs) [7]. In this approach the ink is printed, after which the NPs can be sintered to obtain conductivity. The main material used commercially to date as the metallic NPs is silver. However, the high cost of silver limits the use of silver-based NP inks for low-cost production of conductive patterns. Therefore, inks with other metal NPs, such as copper (that has conductivity properties close to those of silver), are of great interest. However, inks containing copper NPs suffer from stability problems: these NPs are quickly oxidised in ambient conditions. Copper oxides are non-conductive and so the copper particles lose their conducting functionality upon oxidation.

The second approach for producing conductive inks is by Metal Organic Decomposition (MOD) ink. In this approach, a metal organic precursor material is formulated into the ink and printed. In this form, the metal in the metal precursor ink is already in an oxidized form, and therefore, does not undergo oxidation upon contact with oxygen as do some pure metals. If heated under inert conditions, the organic component of the precursor decomposes to volatile components while self-reducing the metal ion, leaving behind a solid conductive metal pattern. Some precursors (or complexes) do not self-reduce, and require a reducing atmosphere during decomposition. Most MOD inks published or presented are in the form of a solution containing metal organic complexes. For example, A. Yabuki and S. Tanaka [8] describe a complex ink of copper formate blended with octylamine and dibutylamine. This ink enabled the printing of copper patterns with 33% bulk copper conductivity after heating at 140°C.

WO 2013/128449 [9] describes a MOD ink that enables the printing of metal conductors. The ink contains a metal-organic salt in the form of oxidation stable nano

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and sub-micron particles. The ink can be printed by various techniques, after which the particles are decomposed. During heating, the organic component decomposes to volatile species while self-reducing the copper ion, leaving behind a solid metal pattern. When preparing a film of the precursor ink and heating to 200°C for 20 minutes a copper film with a sheet resistance of 20 mOhms was obtained.

REFERENCES

- [1] A. Kamyshny, J. Steinke, S. Magdassi, Open Applied Physics Journal 2011, 4.
- [2] H. Li, J. Wu, X. Huang, Z. Yin, J. Liu, H. Zhang, ACS nano **2014**, 8, 6563.
- [3] A. Carlson, A. M. Bowen, Y. Huang, R. G. Nuzzo, J. A. Rogers, Adv. Mater. **2012**, 24, 5284.
- [4] K. Felmet, Y.-L. Loo, Y. Sun, Appl. Phys. Lett. **2004**, 85, 3316.
- [5] US Patent No. 5,246,518.
- [6] US Patent No. 6,105,502.
- [7] J. Perelaer, P. J. Smith, D. Mager, D. Soltman, S. K. Volkman, V. Subramanian, J. G. Korvink, U. S. Schubert, Journal of Materials Chemistry 2010, 20, 8446).
- [8] A. Yabuki and S. Tanaka, Electrically conductive copper film prepared at low temperature by thermal decomposition of copper amine complexes with various amines, 2012.
- [9] WO 2013/128449.

SUMMARY OF THE INVENTION

A general objective of the invention is to provide novel means to indirectly form 2-dimensional (2D) and 3-dimensional (3D) structures and patterns on a surface of a substrate by *Reactive Transfer Printing (RTP)*. This method is utilized for indirectly patterning, coating or forming a thin film of various metals, for example, for fabricating conductive interconnections.

As known in the field, one of the drawbacks associated with fabrication of metallic patterns is that the metallic inks and patterns are prone to oxidation and are therefore relatively unstable. Thus, in order to minimize such deficiencies, the inventors have developed a methodology which permits forming a metallic pattern on a desired surface by first forming a mirror-image pattern of the metallic pattern, the mirror image pattern being formed of precursor materials of the metal composing the metallic pattern

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and causing its decomposition into a metal and transfer of the pattern to the desired surface. It is therefore an objective of the invention to provide a novel method for forming, on a variety of substrates, in particular, heat sensitive substrates, stable, oxidation-resistant metallic patterns or objects. A further objective is to provide an electrically conductive and/or transparent pattern or object on heat sensitive substrates.

The primary advantages of the present invention are, *inter alia*:

(1) the pattern is formed by combining direct printing and direct transfer of the pattern, without the need of a mask; thus, in some embodiments, the method herein being maskless;

(2) the metallic pattern is much less porous than patterns produced using only direct printing methods and thus the resulting pattern is extremely stable;

(3) the process enables forming patterns onto 3D objects, including over sharp and curved angles (including over 90° edges);

(4) the process can be conducted at relatively low temperatures without the need for a vacuum chamber or any costly equipment;

(5) by using digital printing processes various patterns can be obtained;

(6) it can be performed by a continuous process;

(7) it enables overcoming (or partially overcoming) oxidation of the metal deposited on the acceptor substrate, a major problem in utilizing inks based on metallic nanoparticles (for example, inks based on copper formate NPs for obtaining copper metallic nanoparticles pattern); and

(8) since the pattern is formed by direct crystallization of metallic atoms, a very dense layer of the deposited metal is obtained, thus resulting in a pattern having high conductivity (for example, the copper pattern obtained according to one embodiment of the invention provides 50% bulk copper conductivity) without a need for post-printing steps such as sintering,

Thus, the process disclosed herein represents a significant technological step from processes known in the art. The patterning is carried out by transferring the metallic material to a second substrate, rather than direct printing of conductive ink that leads to inferior properties.

To achieve a suitable metallic pattern, a first substrate (referred herein as *donor substrate*) comprising a metal precursor pattern is treated under conditions which cause or permit decomposing of the metal precursor material in the pattern to the

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corresponding metal, the decomposition taking place in close proximity to a second substrate (referred herein as *acceptor substrate*, i.e., the substrate that accepts the metallic pattern), which received the metallic material, thus forming on the second substrate a metallic mirror image of the metal precursor pattern.

The processes of the invention are carried out under reactive transfer printing (RTP) conditions sufficient to permit transfer of the metallic moieties to the second substrate, to thereby form indirectly a metallic pattern on the acceptor substrate. In other words, the desired pattern is printed in a non-direct fashion by transfer of the pattern from a first substrate, having a precursor pattern thereon, to a second substrate.

Thus, in its first aspect, the invention provides a method for indirectly forming a metallic pattern on a surface region of a substrate, the method comprising forming (e.g., by printing or coating) a mirror image of said metallic pattern on a surface region of a first substrate and causing transfer of said pattern to a surface region of a second substrate under conditions of reactive transfer printing (RTP), wherein the mirror image is formed of a metal precursor material.

In a second of its aspects, the invention provides a method for forming a metallic pattern on a substrate, the method comprising applying reactive transfer printing (RTP) conditions to a pair of face-to-face oriented solid surfaces, one of said solid surfaces having on a surface region thereof a pattern of a metal precursor material, whereby a metallic mirror image of said pattern is formed on the other of said solid surfaces upon application of the RTP conditions.

Although a mirror image of the pattern is transferred from the first substrate to the second substrate, the nature of the pattern on the first substrate, prior to initiation of RTP conditions, is different from the pattern obtained on the second substrate after applying said conditions.

The "*surface region*" on which a pattern is formed may be any region or section or area of a substrate surface. In some embodiments, the surface region is a single region or area of the surface. In other embodiments, the term region refers to multiple regions or areas of the substrate surface. In some embodiments, the surface region is a plurality of spaced-apart regions of said substrate, or a continuous region on said substrate, or the full surface of the substrate.

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In some embodiments, where a pattern is formed on two or more regions of a surface, the two or more regions may each be on the same face of the substrate surface or on opposite faces of said substrate.

The regions may be of any predetermined size or shape. The regions may be in the form of a desired predetermined pattern to create a desired structure of products. In some embodiments, the pattern obtained is a conductive pattern. In some embodiments, the pattern is a pattern of electronic interconnections or an electronic circuit. In some embodiments, the pattern or object is an antenna.

The "*metal precursor*" pattern formed on a donor surface is of a material which comprises the metal atom in its oxidized form and which upon RTP conditions gives rise to the metallic form of the same metal (the corresponding metal). In accordance with the invention, the metal precursor may be in the form of a dry powder or liquid ink formulation containing micron, sub-micron particles or nanoparticles. The liquid ink may be in the form of a solution or comprising dissolved precursor or dispersion or large particles, micron particles, sub-micron particles nanoparticles, metal salts, metal complexes, free molecules, or a mixture of these. The dispersion or solution may be aqueous, organic or a water-containing solvent, and may additionally include formulation aides such as dispersion stabilizers, emulsifiers, wetting and rheological additives. The metal atom is in a non-zero oxidation state and is transferable to the zero-oxidation state under the selected RTP process. For example, a copper metal precursor may be copper formate, which upon decomposition under the process of the invention affords the metal copper (Cu^0).

In some embodiments, the metal precursor is in the form of a metal source selected from metal-organic complex, metal-organic salt, metal salt, metal complex particles, metal salt particles and mixtures thereof.

Metal salt or metal salt particles refer to cations of the metallic element which patterning on the surface of a substrate is intended in accordance with the invention. For example, a copper salt refers to a copper cation (e.g., Cu^{2+}) associated with one or more organic and/or inorganic anions (e.g., HCOO^-).

When the metal precursor is a metal source of a metal complex or metal complex particles, the metal complex comprises the metal atom associated with one, two, three or more complexing moieties or chelating moieties. The number of complexing moieties may vary depending, *inter alia*, on the metal atom, its charge, the

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nature of the moiety and the stability of the metal complex. In some embodiments, the metal complex is a metal-organic complex having organic moieties.

In some embodiments, the metal precursor is a metal acetate, metal acetylacetonate, metal ethylhexanoate metal carbonate, metal carboxylate, metal chlorate, metal chloride, metal cyanate, metal nitrate, metal oxalate, metal perchlorate, metal phosphate, metal sulfate, metal sulfite, metal thiocyanate, and metal tetrafluoroborate, as further exemplified hereinbelow.

The particulate metal salt/complex is typically obtained by milling the metal salt/complex material to particulates of a desired size. In some embodiments, milling is achieved by bead milling.

In some embodiments, bead milling is performed by milling a mixture of the metal salt/complex, a stabilizer and a solvent at the presence of beads. The obtained particles may be at the nano range, micron range or at the submicron range. The obtained particle size depends strongly on the milling parameters (bead size, duration, RPM, milling energy input and other parameters), the solid loading, the stabilizer and the solvent.

Alternatively, the metal salt/metal complex particles may be formed by spray drying a solution and precipitation.

Precipitation may also be used to produce the metal salt/complex particles. In such a method, a proper precipitation agent is added to a solution of the precursor material which is allowed to precipitate out. For example, copper formate may be precipitated by addition of formic acid to a copper carbonate solution or dispersion. The copper formate particles precipitate due to their insolubility in the medium. The precipitation process may be performed in the presence of a stabilizer, to control the nucleation and growth of the copper formate particles and to obtain dispersed particles. More specifically, in the case of copper formate particles, the process can be carried out by mixing copper carbonate (or copper acetate) in a proper solvent and thereafter adding formic acid to form copper formate particles, while CO₂ (or acetic acid) is released. Precipitation can also take place by dissolving the copper formate or complexes thereof in a solvent, followed by adding a solvent which does not dissolve copper format.

Generally, the metal salt/metal complex may be in the form of nanoparticles, microparticles or sub-micron particles.

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When the metal salt/metal complex is in the form of nanoparticles, namely, in the form of a particulate material having at least one dimension at the nano-scale, the mean particle size is less than 1,000nm. At times, the metal salt/metal complex is in the form of microparticles, namely, with mean particle size in the range of 0.1 μ m to 100 μ m. Further at times, the metal salt/metal complex is in the form of sub-microparticles, namely, with mean particle size smaller than 1 μ m but larger than 1nm.

In some embodiments, the mean particle size is between about 10nm and 1,000nm. In other embodiments, the mean particle size is between about 50nm and 1,000nm.

In some embodiments, the mean particle size is less than 500nm. In other embodiments, the mean particle size is between about 50nm and 500nm.

In some embodiments, the mean particle size is less than 100nm. In other embodiments, the mean particle size is between about 10nm and 100nm.

In some embodiments, the mean particle size is less than 50 nm. In other embodiments, the mean particle size is between about 10nm and 50nm.

The metal salt/complex particles may have any shape or contour, including spherical and non-spherical shapes (e.g., polyhedral or elongated shape). In some embodiments, the particles have random shapes, or are substantially spherical. In additional embodiments, the particles may be amorphous or crystalline.

In some embodiments, the metal precursor is in a salt form or complex form of a metal element selected from a transition metal, a post-transition metal and a metalloid. In other embodiments, the metal element is selected from Sc, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, Y, Zr, Nb, Tc, Ru, Mo, Rh, W, Au, Pt, Pd, Ag, Mn, Co, Cd, Hf, Ta, Re, Os, Al, Sn, In, Ga and Ir.

In some embodiments, the metal element is selected from Cu, Ni, Ag, Au, Pt, Pd, Al, Fe, Co, Ti, Zn, In, Sn and Ga.

In some embodiments, the metal element is selected from Cu, Ni and Ag.

In some embodiments, the metal element is selected from Ag and Cu.

In some embodiments, said element is Cu.

In some embodiments, the metal precursor is a hydrate of any of the metal precursors described herein. In some embodiments, the metal precursor is in the anhydrous form of any of the metal precursors described herein.

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In some embodiments, the metal precursor comprises an inorganic anion or an organic anion.

In such embodiments, said inorganic anion is selected from HO^- , F^- , Cl^- , Br^- , I^- , NO_2^- , NO_3^- , ClO_4^- , SO_4^{2-} , SO_3^- , PO_4^{2-} and CO_3^{2-} .

In some other embodiments, said organic anion is selected from formate (HCOO^-), acetate (CH_3COO^-), citrate ($\text{C}_3\text{H}_5\text{O}(\text{COO})_3^{-3}$), acetylacetonate, lactate ($\text{CH}_3\text{CH}(\text{OH})\text{COO}^-$), oxalate ($(\text{COO})_2^{-2}$), carboxylates and any derivative thereof.

In some embodiments, the metal precursor is in the form of a salt or complex of copper.

In such embodiments, the copper metal salt or complex is selected from copper formate, copper acetate, copper acetylacetonate, copper oxalate, copper malonate, copper maleate, copper fumarate, copper squarate, copper mellitate and mixtures thereof. In some embodiments, the copper metal salt or complex is copper formate.

In some embodiments, the metal precursor is in the form of a salt or complex of palladium.

In such embodiments, the palladium metal salt or complex is selected from palladium acetylacetonate, palladium acetate, palladium citrate and mixtures thereof.

In some embodiments, the metal precursor is in the form of a salt or complex of tin.

In such embodiments, the tin metal salt or complex is selected from tin chloride and tin ethylhexanoate.

In some embodiments, the metal precursor is in the form of a salt or complex of silver.

In such embodiments, the silver metal salt is selected from silver oxalate, silver lactate, silver formate, silver octanoate and mixtures thereof.

In some other embodiments, the metal precursor is in the form of a salt or complex selected from indium acetate, iron acetate, iron acetylacetonate; gallium acetylacetonate, gallium nitrate; aluminum stearate; silver nitrate; dimethylzinc, diethylzinc; tin acetylacetonate, tin acetate; lead acetate, lead acetylacetonate, and lead nitrate.

As used herein, the "*decomposition*" of the metal precursor material in a metal precursor pattern formed on a donor surface is generally the transformation of the metal cation or metal complex, as exemplified herein, to the metal atom. The decomposition

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pathway or mode may vary based on the type of precursor used, the metal used, the conditions and other parameters.

The "**metallic pattern**" formed on an acceptor substrate is a result of decomposition and transfer (or partial decomposition and transfer) of the original metal precursor pattern, wherein the metallic pattern obtained is deposited on the acceptor substrate as a mirror image of the metal precursor pattern on the first substrate (donor substrate). In other words, the mirror image obtained is reversely arranged in comparison with the original precursor pattern, reversed with reference to an intervening axis or plane, as would appear if the precursor image was viewed in front of a mirror. In some embodiments, the metallic pattern is a metal mesh pattern. In such embodiments, the metal mesh pattern is transparent and conductive.

The processes of the invention are carried out under "**reactive transfer printing (RTP)**" or "**RTP conditions**", namely under conditions sufficient to permit decomposition of the metal precursor material in the precursor pattern and indirect forming of the metallic pattern on the donor substrate. Such conditions include the metal precursor type, mass, particle size and concentration. Further conditions include, the gap size between the first and second substrate, the temperature and pressure applied to the two substrates, the duration of time and the type of gaseous environment. It should be mentioned that the RTP conditions applied depend, *inter alia*, on the metal precursor type, since the RTP conditions depend on the nature of the metal precursor to decompose such that metal atoms are provided to the acceptor substrate.

For achieving efficient transfer of a pattern from the donor surface to the acceptor, the first and second substrates should be closely positioned to one another, in parallel or a face-to-face orientation, such that there is no gap (no space) between them, namely that the two surfaces are intimately contacted, i.e., the gap between them is 0mm, or such that the gap between the surfaces is not greater than 3mm. In other words, the distance between the two surfaces should be between 0 and 3mm.

The first substrate with the precursor pattern thereon and the parallel-positioned second substrate are subjected to sufficient conditions to permit decomposition of the precursor pattern and transfer of metal atoms to the second substrate. These metal moieties migrate (or diffuse) through a transfer pathway to the acceptor substrate, to form thereon, a metallic mirror image of the original metal precursor pattern. During the process, the surface region of the first substrate, typically layered, coated or printed with

a precursor pattern, is placed in close proximity or brought into contact with the second substrate, as generally depicted for certain embodiments in **Fig. 1** and **Fig. 2**.

The method of the invention may be carried out by positioning the first substrate with the precursor pattern above the second substrate and applying RTP conditions, so that the material transfers down to the second substrate. Alternatively, the second substrate may be placed above the first substrate with the precursor pattern and applying RTP conditions, so that the material transfers up to the second substrate (*See Figs. 11A and B*).

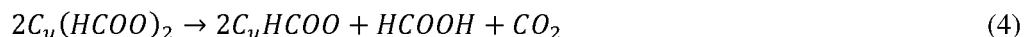
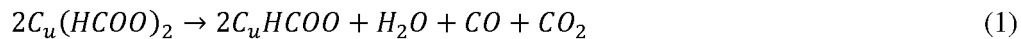
Thus, in some embodiments, the first substrate is positioned on top of the second substrate or the second substrate is positioned on top of the first substrate. It should be emphasized that additional positions may be used, e.g., the positioning may be for different angles of the substrate parallel axis.

A suitable RTP metal precursor is one that is capable of forming volatile metal moieties (i.e., metal atoms) upon decomposition. Such sufficient conditions include, but are not limited to, heating the first and second substrates to a suitable temperature and for a sufficient time, applying an inert gas (e.g., nitrogen, argon), pressure and the positioning of the second substrate relative to the first substrate, to thereby convert the metal cation/complex in the precursor into metal atoms.

For example, copper formate is suitable since upon its decomposing, volatile copper moieties are formed. Without being bound by theory, copper decomposes through two successive steps of cation reduction. The first decomposition/reduction step results in copper moieties that migrate through the gas phase to the acceptor. On the acceptor substrate the copper moieties undergo the second decomposition/reduction step, resulting in the deposition of pure copper, forming a copper mirror image, with excellent conductivity. Namely, the first decomposition/reduction step results in a smaller volatile metal organic molecule. The volatility is exploited to enable diffusion via the gas phase to a near-by substrate where it further decomposes in the second reduction step and copper is deposited.

The mechanism of the copper pattern formation was investigated (i.e., decomposition process of the copper formate ink upon heating) by DSC and TGA coupled with MS (Simultaneous thermal analysis - Mass spectrometer, *See Fig. 4*). Without wishing to be bound by theory, the decomposition process of copper formate to copper metal involves the following steps:

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The detection of water by MS indicates the occurrence of Equation (1). The absence of copper (I) formate in the MS results is probably due to the fast reduction to Cu^0 according to Equation (2), yet it is believed it should be formed since Equation (1) is the most likely possibility to form water.

It should be emphasized that the methods of the invention do not all involve the above suggested mechanism. Other metals may be decomposed and transferred by different mechanisms according to the methods disclosed herein.

Thus, the precursor material may react completely or only partially, for example if the reaction is by decomposition, transfer can occur even if the precursor only partially decomposes. In addition, during the process, part of the precursor material may be left on the donor substrate, such as in the case of copper formate. If the donor material of a metal transfers partially, the remaining metal can be recovered and recycled, e.g., by hydrometallurgy. The partial transfer of the precursor pattern is displayed in **Fig. 9**, showing the percent of copper transferred from the donor substrate to the acceptor substrate depending on the gap between the substrates.

Thus, in some embodiments, the metallic pattern comprises at least 20% w/w elemental metal (i.e., metal atoms) out of the initial weight percent of the same metal in the precursor pattern, in some embodiments, at least 30%, at least 35%, at least 40% or at least 50% w/w elemental metal (i.e., metal atoms) out of the initial weight percent of the same metal in the precursor pattern. In some embodiments, the metallic pattern comprises at least 20, 21, 22, 23, 24, 25, 26, 27, 28, 29, 30, 31, 32, 33, 34, 35, 36, 37, 38, 39, 40, 41, 42, 43, 44, 45, 46, 47, 48, 49 or 50% w/w elemental metal (i.e., metal atoms) out of the initial weight percent of the same metal in the precursor pattern.

In some embodiments, the metal precursor is thus selected amongst such precursors which decompose at a temperature lower than the melting point of the substrates' material.

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In some embodiments, the metal precursor is selected to decompose at a temperature lower than 300°C, lower than 250°C, lower than 200°C, or lower than 150°C.

In some embodiments, the metal precursor is selected to decompose at a temperature between 20°C to 300°C, between 50°C to 300°C, between 100°C to 300°C, between 20°C to 250°C, between 50°C to 250°C, between 100°C to 250°C, between 150°C to 300°C, or between 150°C to 250°C. In some embodiments, said temperature is at most 200°C.

In some embodiments, the reactive transfer printing (RTP) conditions are applied for a time and at a temperature sufficient to cause decomposition of the metal precursor.

The decomposition of the metal precursor may be carried out by heating or by applying any other process conditions which result in the transformation of the metal cations/complexes in the precursor metallic pattern into the corresponding metal atoms. The heating may be carried out under nitrogen, argon, vacuum or under a non-oxidizing (inert) atmosphere. In some embodiments, the decomposition is carried out under reducing atmosphere. In some embodiments, decomposition is achievable by heating under air.

In some embodiments, said decomposition is carried out under gas flow. In some embodiments, the gas flow is sufficient to permit a transfer pathway for transferring a pattern and deposition of a mirror image of the pattern on a second substrate. In some embodiments, the gas flow is nitrogen, argon or any other inert gas that affords an inert environment.

The conversion from the salt (metal cations) or complex form to the metallic form may be carried out by heating, e.g., in an oven, by laser radiation, by microwave, by electrical voltage, by exposure to light (such as IR, UV, Vis, Xenon); by photonic curing (e.g., flash lamp, laser), by RF radiation, microwave radiation or by plasma treatment or any other method which permits decomposition to the metallic form.

In some embodiments, said decomposing is achieved by thermal heating, laser heating, microwave heating, electrical voltage heating, or heating by exposure to light.

In some embodiments, said decomposition is thermal decomposition.

The process can be implemented using a method in which a thin film of the donor material is placed on, e.g., a ribbon, which is heated at specific areas, causing the

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transfer of material to an acceptor substrate at specific areas, resulting in a pattern on the acceptor substrate. For example, the patterning can be carried out directly on the ribbon with the film by applying localized heat by a laser. Thus, in some embodiments, the heating is carried out on a specific part/region of the substrate.

An additional variation of the process of the invention is printing a pattern on a dry precursor film, resulting in decomposition or removal of the material (depending on the heating settings, e.g., by laser, substrate and precursor material), thus leaving a precursor film with a pattern in which the graphics do not contain the precursor. For example, **Fig. 14A** shows a copper formate film with such a pattern. This pattern is transferred to a second glass slide under RTP conditions, thus resulting with an obtained pattern comprising a film with the engraved pattern (shown in **Fig. 14B**).

The decomposition and conversion of the metal precursor into a metal may be carried out also by chemical methods. For example, deposition and contact (by printing or other methods) of a reducing agent or any other chemical that can lead to the formation of the metallic pattern.

In some embodiments, said decomposition is carried out at atmospheric pressure or at moderate pressure, i.e., between 0.001atm to 100atm, or 0.5atm to 2atm.

In some embodiments, said decomposition is carried out under an inert atmosphere (e.g., nitrogen or argon at a pressure of 0.001atm to 100atm, at times between 0.5atm to 2atm), vacuum, reducing gas, or in air.

The printed layers of metal precursors may be added or combined with other layers, for example, metallic particles. This can be achieved either by using a metal precursor that contains both metallic particles and the insoluble particles or complexes, or mixtures thereof, or by printing several materials in a successive process, i.e., indirect printing of the different layers consecutively.

The patterns may be printed on flexible or rigid substrates, a variety of plastics such as Nylon, PET, PEN, polycarbonate, Teslin, PVC and others, paper, glass, metallic surfaces, semiconductors such as silicon, germanium, ITO, FTO, TiO₂ and others.

For example, a thin film or pattern (i.e., precursor film or pattern) can be applied on a curved or flexible donor substrate (e.g., aluminium foil) and a 3D object (acceptor object) can be wrapped or coated with this flexible substrate, after which the pattern may be induced to transfer under RTP conditions.

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In some embodiments, the first and second substrates, independently, are composed of a material selected from plastic, fabric, glass, glass fibers, composite material, laminates such as CEM-1 (composite epoxy material), FR-4 and G-10 (glass epoxy materials/fiberglass), metal, alloy, metal oxide, semiconductor, ceramic, quartz, silicon, germanium, ITO, FTO and TiO₂.

In some embodiments, said first substrate or second substrate, independently, is of a material selected from glass, plastic, silicon and metal. In such embodiments, said metal is selected from Al, Ni, Cu, Au, Ag, Ti, Pd and Pt. In some embodiments, said metal is Al.

In some embodiments, said first substrate and second substrate, independently, are each composed of a different material.

In some embodiments, said first substrate and second substrate, independently, are composed of the same material.

In some embodiments, said first substrate or second substrate, independently, is a flexible substrate or a rigid substrate, capable of withstanding the reactive transfer printing conditions (RTP).

In some embodiments, said plastic is a heat-resistant plastic. In such embodiments, said heat-resistant plastic is selected from polyethylene naphthalate-PEN, polyethylene terephthalate-PET and polyimide (Kapton). In some embodiments, the heat resistant plastic is any plastic substrate that is not deformed under the RTP temperature.

As abovementioned, a suitable RTP metal precursor according to the invention disclosed herein is one that is capable of forming volatile metal moieties (i.e., metal atoms or other metal precursors) upon decomposition.

The metal precursor pattern may be obtained by, e.g., printing or coating a pattern using an ink containing an RTP suitable precursor on a donor substrate as a mirror image of the desired metallic pattern. The pattern of a metal precursor material may be formed by conventional printing techniques. Some non-limiting printing techniques are ink-jet printing, screen printing, offset, gravure, flexography and laser printing.

Thus, in a further aspect, the invention provides a method of fabricating a metallic pattern (or patterned object) on a surface region of a substrate, the method comprising:

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bringing into close proximity or contact a surface region of a first substrate with a surface region of a second substrate, wherein the surface region of the first substrate having a pattern thereon of at least one metal precursor material,

the method being carried out under reactive transfer printing (RTP) conditions, to allow decomposition of the at least one metal precursor material in the pattern and transfer of the decomposed at least one metal precursor material to a surface region of the second substrate, whereby a metallic pattern is formed on the second substrate.

In some embodiments, the invention also provides, as an initial step, forming of the precursor pattern on a surface of the first substrate before the step of bringing into contact a surface region of the first substrate with a surface region of the second substrate.

Thus, in some embodiments, the method comprises:

- a) forming a pattern of at least one metal precursor material on a surface region of the first substrate;
- b) bringing into close proximity or contact a surface region of the first substrate having a pattern thereon with a surface region of the second substrate;
- c) applying reactive transfer printing (RTP) conditions, to thereby allow decomposition of the at least one metal precursor material in the pattern and transfer of the decomposed at least one metal precursor material to a surface region of the second substrate, whereby a metallic pattern is formed on the second substrate.

In some embodiments, the method described herein, further comprising a step of obtaining an ink formulation comprising at least one metal precursor material; and forming the pattern of at least one metal precursor material on a surface region of the first substrate. In some embodiments, the thickness of the pattern of at least one metal precursor material on a surface region of the first substrate is at times between 0.005 μ m to 4mm, at times between 0.01 μ m to 2mm, at times between 0.01 μ m to 1mm, at times between 0.005 μ m to 1mm, at times between 0.01 μ m to 0.5mm, at times between 0.01 μ m to 0.1mm, and further at times between 0.01 μ m to 50 μ m.

In some embodiments, the method further comprises pretreating the first substrate or second substrate prior to applying RTP conditions. At times, the pretreating of any one of the substrates is required, independently, in order to cause activation of the substrates to permit sufficient adhesion of the metal precursor pattern on the

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acceptor substrate, or in order to permit sufficient adhesion of the metallic pattern on the donor substrate. The pretreatment process may be any pretreatment process known in the art, such as, but not limited to plasma treatment, annealing and chemical etching.

As appreciated, the method steps may be repeated such that a further layer of a metal precursor is formed on the obtained layer of the metallic layer in order to modify its thickness and/or height.

Thus, the methods of the invention can be implemented using a continuous process in which several types of materials can be used so as to pattern different types of metals, insulators and semiconductors to fabricate electrical devices. The patterning of different compounds on the acceptor substrate can be carried out by a single decomposition step after all the donor patterns are printed. Alternatively, it can be carried out by transferring and depositing the different materials in consequence steps.

In some embodiments, the method described herein comprises forming, e.g., printing and coating, a metal precursor pattern on a surface region of a first substrate.

The metal precursor may be in the form of a dry powder or liquid. In some embodiments, said metal precursor (i.e., ink or printing formulation) is formulated as a dispersion, in which the material is substantially insoluble in a liquid medium; or solution, in which the metal precursor is dissolved in a liquid medium. The medium may be an aqueous or non-aqueous (organic) liquid medium.

In some embodiments, said liquid medium is an aqueous medium or organic medium. In other embodiments, the medium may be an organic solvent or a medium containing an organic solvent. In some embodiments, the organic medium or solvent is selected from glycol, glycol ether, alcohol, acetate, amides, hydrocarbons and mixtures thereof. In some embodiments, the organic medium or solvent is selected from glycol, glycol ether, alcohol, acetate and mixtures thereof.

In some embodiments, the organic medium comprises a glycol ether.

In some embodiments, the medium is selected from dipropylene glycol methyl ether (DPM), 2-methoxyethyl ether (diglyme), triethyleneglycol dimethyl ether (triglyme), propylene glycol, sulfolane, polyethylene glycol and glycerol.

In some embodiments, the organic solvent is selected amongst glycol ethers. In some embodiments, the glycol ether is selected from Dowanol™ DB, Dowanol™ PM glycol ether, Dowanol™ DPM, Dowanol™ DPM glycol ether, Dowanol™ DPMA glycol ether, Dowanol™ TPM glycol ether, Dowanol™ TPM-H GE, Dowanol™ PMA,

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DowanolTM DPMA, DowanolTM PnP glycol ether, DowanolTM DPnP glycol ether, DowanolTM PnB glycol ether, DowanolTM DPnB glycol ether, DowanolTM TPnB glycol ether, DowanolTM PPh glycol ether, DowanolTM PGDA, DowanolTM DMM, DowanolTM EPh glycol ether, and any other glycol ether. In the above list, DowanolTM are DOW Chemical Co. hydrophobic/hydrophilic glycol ethers.

In other embodiments, the solvent is an alcohol selected from methanol, ethanol, propanol, butanol and other alcohols. In further embodiments, the solvent may be acetate such as ethyl acetate, ethylaceto acetate, and others.

In other embodiments, the solvent is selected from diethyl ether, acetone, ethyl acetate, ethanol, propanol, butanol, and any combination thereof.

The metal salt/complex particles of the precursor material may be stabilized by one or more stabilizers (dispersing agents, dispersants) to prevent aggregation and/or agglomeration of the particles and to enable a stable dispersion. Such materials may be a surfactant and/or a polymer. The stabilizer may have ionic or non-ionic functional groups, or a block co-polymer containing both. It may also be a volatile stabilizer which evaporates during the decomposition of the metal salt; thus enabling higher conductivities after the decomposition and sintering of the pattern. That stabilizer may additionally be selected to have the ability of forming a complex with the metal.

In some embodiments, said metal precursor formulation further comprises a material selected from a solvent, a stabilizing agent, a surfactant, a binder, a humectant, a wetting agent and mixtures thereof.

In some embodiments, the stabilizing agent is the dispersion medium itself.

The dispersing agent may be selected amongst surfactants, capping agents, polyelectrolytes or polymeric materials. Representative examples of such dispersants include without limitation polycarboxylic acid esters, unsaturated polyamides, polycarboxylic acids, polycarboxylate, alkyl amine salts of polycarboxylic acids, polyacrylate dispersants, polyethyleneimine dispersants, polyethylene oxide, and polyurethane dispersants and co-polymers of these polymers.

In some embodiments, the dispersant is selected without limitation from:

- Disperse BYK® 190, Disperse BYK® 161, Disperse BYK® 180, Disperse BYK® 9076, Disperse BYK® 163, Disperse BYK® 164, Disperse BYK® 2000 and Disperse BYK® 2001, all of which being available from BYK;

- EFKA® 4046 and EFKA® 4047, available from EFKA;

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- Solsperse® 40000, Solsperse® 39000 and Solsperse® 24000 available from Lubrizol; and polyvinyl pyrrolidone (PVP) of various molecular weights.

In further embodiments, the dispersant is a surfactant, which may or may not be ionic. In some embodiments, the surfactant is cationic or anionic. In further embodiments, said surfactant is non-ionic or zwitterionic. Non-limiting examples of such cationic surfactants include didodecyldimethylammonium bromide (DDAB), CTAB, CTAC, cetyl(hydroxyethyl)(dimethyl)ammonium bromide, N,N-dimethyl-N-cetyl-N-(2-hydroxyethyl)ammonium chloride, anionic surfactants such as sodium dodecyl sulfate (SDS) and various unsaturated long-chain carboxylates, zwitterionic phospholipids, such as 1,2-bis(10,12-tricosadiynoyl)-sn-glycero-3-phosphocholine, water-soluble phosphine surfactants, such as sodium salts of sulfonated triphenylphosphine, $P(m-C_6H_4SO_3Na)_3$ and alkyltriphenyl-methyltrisulfonate, $RC(p-C_6H_4SO_3Na)_3$, alkyl polyglycol ethers, e.g., ethoxylation products of lauryl, tridecyl, oleyl, and stearyl alcohols; alkyl phenol polyglycol ethers, e.g., ethoxylation products of octyl- or nonylphenol, diisopropyl phenol, triisopropyl phenol; alkali metal or ammonium salts of alkyl, aryl or alkylaryl sulfonates, sulfates, phosphates, and the like, including sodium lauryl sulfate, sodium octylphenol glycoether sulfate, sodium dodecylbenzene sulfonate, sodium lauryldiglycol sulfate, and ammonium tri-tert-butyl phenol and penta- and octa-glycol sulfonates; sulfosuccinate salts, e.g., disodium ethoxylated nonylphenol ester of sulfosuccinic acid, disodium n-octyldecyl sulfosuccinate, sodium dioctyl sulfosuccinate, and the like.

In some embodiments, the stabilizing agent is a cationic polymer.

In some embodiments, the stabilizing agent is selected from a polyelectrolyte, a polymeric material, a cationic surfactant, an anionic surfactant, a non-ionic surfactant, a zwitterionic surfactant and a cationic polymer.

In some embodiments, said metal precursor being in the form of metal salt nanoparticles or sub-micron particles of copper formate dispersed in glycol ether, and further comprising a stabilizer being a functionalized polymer.

In some embodiments, the metal precursor is copper formate, the solvent being glycol ether and the stabilizer being a functionalized polymer. In some embodiments, the stabilizing agent is a copolymer or salt of a copolymer having acidic groups.

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The printing formulation may further comprise an additive selected from humectants, binders, surfactants, fungicides, rheology modifiers, pH adjusting agents, wetting agents and mixtures thereof.

In order to obtain a metallic pattern or object having sufficient height and size, or for obtaining a metallic pattern comprising multiple layers of the same or different metal, the methods of the invention disclosed herein may be carried out repetitively by printing several layers of one or more metallic patterns on each other. In some embodiments, the forming a metallic pattern on a substrate is by forming at least one layer of metal, said layer being composed of at least one metal source. In some embodiments, the metal source is selected to be any one of the metals recited above.

The printing of the donor may be performed by a variety of printing technologies such as screen and inkjet printing.

It should be understood that the layer of metal precursor need not be formed (or pre-formed) on the whole surface region of the material. Typically, the precursor pattern may be formed to have a desired shape and a desired thickness, to be composed of a desired selection of metal moieties, such that the deposited metal pattern will be of a desired shape and thickness. It should be further noted that the RTP method can be used as a substitute for sputtering to deposit continuous layers of metal, such as copper, on a substrate without needing to operate under vacuum. This, for example, may be utilized in coating plastic substrates with thin layer of copper to impart antimicrobial properties.

The surface region comprising a metal precursor pattern is reacted with a surface region of the second material to form thereon a layer or a coat, the shape of which being determined by the shape of the original precursor pattern which composition and thus properties are to be controlled under RTP conditions. As used herein, the pattern may be a monolayer, a bi-layer, a multi-layer, a thin film, a layer or any form of assembly of the metal atoms.

One of the major challenges in printing metal-based conductive patterns, e.g., copper patterns, is the stability of the metallic inks and patterns, prior to and after sintering. In the present invention the metal precursor is selected to be resistant to oxidation, and so the ink is stable for prolonged time periods. The pattern obtained after the decomposition process, as disclosed hereinbelow, is highly stable in air. This is due to the highly dense packing the pattern and the presence of medium-large grains that are

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closely-packed to one another. The presence of medium-large grains in combination with the highly dense surface increased oxidation resistance of the copper surface. **Fig. 5** presents HR-SEM images of the surface of the obtained pattern after decomposition and transfer, demonstrating the unique highly dense packing. In some cases, a more continuous and dense film is obtained as the gap between the substrates decreases, as can be seen for gaps of 1mm, 0.6mm, and 0.1mm (**Fig. 5D** to **Fig. 5F**). The morphology structure of the copper transferred according to the processes of the present disclosure without a gap (a distance of 0mm, **Fig. 5G**), is highly continuous. These results display further advantage of the process of the present invention, namely, the ability to obtain a continuous and dense layer of the transferred material. Thus, in some embodiments, the morphology of the pattern is substantially continuous. Namely, the image of the morphology of the structure obtained (e.g., by SEM or HR-SEM imaging) above comprises a percentage of voids (i.e., density of voids) within the structure below 95%, at times, below 90%, at times, below 85%, and further at times, below 80%.

In some embodiments, the pattern having essentially no voids (or gaps) between particle grains when observed at a magnification revealing structures above about 500nm, for example, as shown in **Fig. 19D**. Thus in accordance with this embodiment, the particles are very closely associated with each other such that gaps (voids), if any, are of a size (width) of less than 0.1 μ m. While not wishing to be bound by theory, this is achieved by applying the method of the invention under RTP conditions sufficient for forming a metallic pattern, including the condition of a close-enough gap between the donor and acceptor substrates to enable the desired patterning with essentially no gaps between the formed particle or grains.

It should be emphasized that other methods for forming metallic patterns of the art exhibit lower conductivities and lower resistance to oxidation. **Fig. 6** shows that even after one year of manufacture of a copper pattern according to the processes of the invention, did not exhibit any oxides detected by XRD, thus demonstrating that the sample is highly stable against oxidation. **Fig. 7** shows that the copper pattern obtained according to one embodiment of the method of the invention, is of 230nm height and exhibited very low resistance. As such, lower resistivity, i.e., higher conductivity is obtained for the patterns provided by the present invention.

Thus, in some embodiments, the pattern or object obtained is electrically conductive. In some embodiments, the conductivity of the metallic pattern is above 70%

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of the bulk conductivity of the metal, at times, the conductivity of the metallic pattern is above 60% of the bulk conductivity of the metal, at times, the conductivity of the metallic pattern is above 50% of the bulk conductivity of the metal, at times, the conductivity of the metallic pattern is above 33% of the bulk conductivity of the metal, at times, above 10% of the bulk conductivity of the metal, and further at times, the conductivity of the metallic pattern is above 1% of the bulk conductivity of the metal.

In some embodiments, the resistivity of the metallic pattern is in the range of $1.0 \cdot 10^{-8} \Omega\text{m}$ to $2.0 \cdot 10^{-6} \Omega\text{m}$, at times, the resistivity of the metallic pattern is in the range of $1.7 \cdot 10^{-8} \Omega\text{m}$ to $1.0 \cdot 10^{-6} \Omega\text{m}$.

In another aspect of the invention is provided a method of converting a patterned metal precursor material into a metallic pattern, the method comprising:

forming a pattern of at least one metal precursor material on a surface region of a substrate; and

causing conversion of the metal precursor material to a metallic material under RTP conditions.

In some embodiments, the metallic material is formed on a different substrate.

In yet another aspect of the invention is provided a pattern or object obtainable by the method disclosed herein.

In some embodiments, the pattern or object obtained is electrically conductive or transparent, for example a pattern composed of metal oxide. Non-limiting examples of the metal oxide may be one or more of the following: SnO_2 with dopant as: Sb, F, As, Nb, Ta; In_2O_3 with dopant as: Sn, Ge, Mo, F, Ti, Zr, Hf, Nb, Ta, W, Te; ZnO with dopant as: Al, Ga, B, In, Y, Sc, F, V, Si, Ge, Ti, Zr, Hf; CdO with dopant as: In, Sn, ZnO– SnO_2 , Zn_2SnO_4 , ZnSnO_3 ; ZnO– In_2O_3 , $\text{Zn}_2\text{In}_2\text{O}_5$, $\text{Zn}_3\text{In}_2\text{O}_6$; In_2O_3 – SnO_2 , $\text{In}_4\text{Sn}_3\text{O}_{12}$, CdO– SnO_2 , Cd_2SnO_4 , CdSnO_3 ; CdO– In_2O_3 , CdIn_2O_4 ; MgIn_2O_4 ; GaInO_3 , $(\text{Ga}, \text{In})_2\text{O}_3$ with dopant as: Sn, Ge; CdSb_2O_6 with dopant as: Y; ZnO– In_2O_3 – SnO_2 , $\text{Zn}_2\text{In}_2\text{O}_5$ – $\text{In}_4\text{Sn}_3\text{O}_{12}$; CdO– In_2O_3 – SnO_2 , CdIn_2O_4 – Cd_2SnO_4 ; ZnO–CdO– In_2O_3 – SnO_2 .

In some embodiments, the conductive pattern or object disclosed herein, is substantially free of metal oxide.

In yet another aspect there is provided an element comprising a pattern or an object.

In some embodiments, the pattern or object described herein, for use in producing an element on an electronic device or optoelectronic device.

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In some embodiments, the element is associated with an electric circuit or conductive interconnections. The association refers to the element being part of or linked to an electronic circuit or conductive interconnections.

In another of its aspects, the invention provides a device comprising a pattern or object or an element. In some embodiments, the device is an electronic device or optoelectronic device.

The method of the present invention may be widely used for obtaining patterns for various applications including, but not limited to, electronic, optoelectronic, medical devices, art articles and jewelry. In some embodiments, the metal patterns are shiny. In some embodiments, the method disclosed herein for EMI shielding materials, conductive adhesives, low-resistance metal wirings, PCBs, FPCs, antennas for RFID tags, solar cells, secondary cells or fuel cells and electrodes or wiring materials for TFT-LCDs, OLEDs, flexible displays, OTFTs, sensors and others.

In some embodiments, the metallic pattern is a shiny metal pattern.

In some embodiments, the method disclosed herein may also be applied for patterning non-conductive materials.

The invention further provides a kit comprising at least one solid surface having on at least a region thereof a pattern of a metal precursor material, the material being suitable for forming a mirror image of said pattern on a different substrate, and instructions of use. In some embodiments, the instructions related to use of the solid surface are in accordance with RTP conditions disclosed herein.

In some embodiments, the kit comprises a pair of solid surfaces, one of which having on at least a region thereof a pattern of a metal precursor material, the material being suitable for forming a mirror image of said pattern on the other of said pair of solid surfaces, and instructions of use.

In some embodiments, each solid surface of the pair of solid surfaces is different. In some embodiments, one of the surfaces is a solid acceptor substrate and the other is a ribbon having a pattern of a metal precursor material printed thereon.

The invention further provides a pair of solid surfaces, one of which having on at least a region thereof a pattern of a metal precursor material, the material being suitable for forming a mirror image of said pattern on the other of said pair of solid surfaces, wherein the pair of surfaces are intimately provided in a configuration ready for RTP.

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All amounts or measures indicated below with the term "*about*" followed by a number should be understood as signifying the indicated number with a possible tolerance between approximately 10% above the indicated number and 10% below that number.

EMBODIMENTS OF THE INVENTION

The following is a list of embodiments of the invention:

A method for indirectly forming a metallic pattern on a surface region of a substrate, the method comprising forming a mirror image of said metallic pattern on a surface region of a first substrate and causing transfer of said pattern to a surface region of a second substrate under conditions of reactive transfer printing (RTP), wherein the mirror image is formed of a metal precursor material.

A method for forming a metallic pattern on a substrate, the method comprising applying reactive transfer printing (RTP) conditions to a pair of face-to-face oriented solid surfaces, one of said solid surfaces having on a surface region thereof a pattern of a metal precursor material, whereby a metallic mirror image of said pattern is formed on the other of said solid surfaces upon application of the RTP conditions.

A method for fabricating a metallic pattern on a surface region of a substrate, the method comprising:

bringing into close proximity or contact a surface region of a first substrate with a surface region of a second substrate, wherein the surface region of the first substrate having a pattern thereon of at least one metal precursor material,

the method being carried out under reactive transfer printing (RTP) conditions, to allow decomposition of the at least one metal precursor material in the pattern and transfer of the decomposed at least one metal precursor material to a surface region of the second substrate, whereby a metallic pattern is formed on the second substrate.

A method comprising:

a) forming the pattern of at least one metal precursor material on a surface region of the first substrate;

b) bringing into close proximity or contact the surface region of the first substrate having a pattern thereon with a surface region of the second substrate;

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c) applying reactive transfer printing (RTP) conditions, to thereby allow decomposition of the at least one metal precursor material in the pattern and transfer of the decomposed at least one metal precursor material to a surface region of the second substrate, whereby a metallic pattern is formed on the second substrate.

A method further comprising obtaining an ink formulation comprising at least one metal precursor material; and forming the pattern of at least one metal precursor material on a surface region of the first substrate.

A method wherein the thickness of the pattern of at least one metal precursor material on a surface region of a first substrate is between 0.01 μ m to 1mm.

A method further comprising pretreating the first substrate or second substrate prior to applying RTP conditions.

A method wherein decomposing is achieved by thermal heating, laser heating, microwave heating, electrical voltage heating, or heating by exposure to light.

A method wherein said decomposition is thermal decomposition.

A method wherein decomposing is achieved by photonic curing, UV radiation, IR radiation or by plasma treatment.

A method wherein decomposing is achieved by heating under air, nitrogen, argon or a non-oxidizing atmosphere.

A method wherein decomposing is achieved by heating under a non-oxidizing atmosphere.

A method wherein said non-oxidizing atmosphere is nitrogen or argon.

A method wherein reactive transfer printing (RTP) conditions are applied for a time and at a temperature sufficient to cause decomposition of the metal precursor.

A method wherein said temperature is between 20°C to 300°C.

A method wherein said temperature is between 150°C to 250°C.

A method wherein said temperature is at most 200°C.

A method wherein the decomposition step is carried out at atmospheric pressure.

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A method wherein said first substrate and second substrate are each of a different material.

A method wherein said first substrate and second substrate are composed of the same material.

A method wherein said first substrate or second substrate is a flexible substrate or a rigid substrate, capable of withstanding the reactive transfer printing conditions (RTP).

A method wherein said substrate is of a material selected from plastic, fabric, composite material, laminates, glass, metal, alloy, metal oxide, semiconductor, ceramic, quartz, silicon, germanium, ITO, FTO and TiO_2 .

A method wherein said first substrate or second substrate is of a material selected from glass, plastic, silicon and metal.

A method wherein said plastic is a heat-resistant plastic.

A method wherein said at least one metal precursor material is in the form of a metal source selected from metal-organic complex, metal-organic salt, metal salt, metal complex particles, metal salt particles and mixtures thereof.

A method wherein said at least one metal precursor material is in a salt form or complex form of an element selected from a transition metal, a post-transition metal and a metalloid.

A method wherein said element is selected from Sc, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, Y, Zr, Nb, Tc, Ru, Mo, Rh, W, Au, Pt, Pd, Ag, Mn, Co, Cd, Hf, Ta, Re, Os, Al, Sn, In, Ga and Ir.

A method wherein said element is selected from Cu, Ni, Ag, Au, Pt, Pd, Al, Fe, Co, Ti, Zn, In, Sn and Ga.

A method wherein said element is selected from Cu, Ni and Ag.

A method wherein said element is selected from Ag and Cu.

A method wherein said element is Cu.

A method wherein said metal precursor comprises an inorganic anion or an organic anion.

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A method wherein said inorganic anion is selected from HO^- , F^- , Cl^- , Br^- , I^- , NO_2^- , NO_3^- , ClO_4^- , SO_4^{2-} , SO_3^- , PO_4^- and CO_3^{2-} .

A method wherein said organic anion is selected from formate (HCOO^-), acetate (CH_3COO^-), citrate ($\text{C}_3\text{H}_5\text{O}(\text{COO})_3^{3-}$), acetylacetonate, lactate ($\text{CH}_3\text{CH}(\text{OH})\text{COO}^-$), oxalate ($(\text{COO})_2^{2-}$), carboxylates and any derivative thereof.

A method wherein the metal precursor is in the form of a salt or complex of copper.

A method wherein the copper metal salt or complex is selected from copper formate, copper acetate, copper acetylacetonate, copper oxalate, copper malonate, copper maleate, copper fumarate, copper squarate, copper mellitate and mixtures thereof.

A method wherein the copper metal salt or complex is copper formate.

A method wherein the metal precursor is in the form of a salt or complex of palladium.

A method wherein the palladium metal salt or complex is selected from palladium acetylacetonate, palladium acetate, palladium citrate, and mixtures thereof.

A method wherein the metal precursor is in the form of a salt or complex of tin.

A method wherein the tin metal salt or complex is selected from tin chloride and tin ethylhexanoate.

A method wherein the metal precursor is in the form of a salt or complex of silver.

A method wherein the silver metal salt is selected from silver oxalate, silver lactate, silver formate, silver octanoate and mixtures thereof.

A method wherein the metal precursor is in the form of a salt or complex selected from indium acetate, iron acetate, iron acetylacetonate; gallium acetylacetonate, gallium nitrate, aluminum stearate; silver nitrate, dimethylzinc, diethylzinc, tin acetylacetonate, tin acetate; lead acetate, lead acetylacetonate, and lead nitrate.

A method wherein the metal precursor is selected to be convertible into a metal atom by a decomposition process.

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A method wherein said metal precursor is in liquid form or in powder form.

A method wherein said metal precursor is formulated as dispersion or solution in a liquid medium.

A method wherein said liquid medium is an aqueous medium or organic medium.

A method wherein said organic medium is selected from glycol ether, alcohol, acetate and mixtures thereof.

A method wherein said organic medium comprises glycol ether.

A method wherein said metal precursor formulation further comprises a material selected from a solvent, a stabilizing agent, a surfactant, a binder, a humectant and a wetting agent, and mixtures thereof.

A method wherein the stabilizing agent is selected from a polyelectrolyte, a polymeric material, a cationic surfactant, an anionic surfactant, a non-ionic surfactant, a zwitterionic surfactant and a cationic polymer.

A method wherein said metal precursor being in the form of metal salt nanoparticles or sub-micron particles of copper formate dispersed in glycol ether, and further comprising a stabilizer being a functionalized polymer.

A method further comprising a step of sintering the metallic pattern.

A method wherein the first substrate and said second substrate are placed at a distance of between 0 and 3mm.

A method wherein the pattern or object obtained is electrically conductive.

A method wherein the pattern or object obtained is transparent.

A method wherein the conductivity of the metallic pattern is above 70% of the bulk conductivity of the metal.

A method wherein the conductivity of the metallic pattern is above 50% of the bulk conductivity of the metal.

A method wherein the conductivity of the metallic pattern is above 33% of the bulk conductivity of the metal.

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A method wherein the conductivity of the metallic pattern is above 10% of the bulk conductivity of the metal.

A method wherein the conductivity of the metallic pattern is above 1% of the bulk conductivity of the metal.

A method wherein the resistivity of the metallic pattern is in the range of $1.0 \cdot 10^{-8} \Omega\text{m}$ to $2.0 \cdot 10^{-6} \Omega\text{m}$.

A method wherein the resistivity of the metallic pattern is in the range of $1.7 \cdot 10^{-8} \Omega\text{m}$ to $1.0 \cdot 10^{-6} \Omega\text{m}$.

A method of converting a patterned metal precursor material into a metallic pattern, the method comprising:

forming a pattern of at least one metal precursor material on a surface region of a substrate; and

causing conversion of the metal precursor material to a metallic material under RTP conditions.

A method wherein the metallic material is formed on a different substrate.

A pattern or object obtainable by a method herein.

A pattern or object being electrically conductive or transparent.

A conductive pattern or object being substantially free of metal oxide at the time of manufacture.

A pattern or object for use in producing an element on an electronic device or optoelectronic device.

A pattern or object wherein the element is associated with an electric circuit or conductive interconnections.

An element comprising a pattern or object disclosed herein.

A device comprising a pattern or object disclosed herein or an element disclosed herein.

A device being an electronic device or optoelectronic device.

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A kit comprising at least one solid surface having on at least a region thereof a pattern of a metal precursor material, the material being suitable for forming a mirror image of said pattern on a different substrate, and instructions of use.

A kit wherein the instructions related to use of the solid surface are in accordance with RTP conditions.

BRIEF DESCRIPTION OF THE DRAWINGS

In order to better understand the subject matter that is disclosed herein and to exemplify how it may be carried out in practice, embodiments will now be described, by way of non-limiting example only, with reference to the accompanying drawings, in which:

Figs. 1A-D. RTP process scheme according to an embodiment of the invention, where: **(A)** shows a donor substrate with printed pattern; **(B)** shows an acceptor substrate placed above the donor substrate with a gap between them maintained by a spacer; **(C)** shows two substrates after decomposition showing the obtained pattern on the acceptor substrate; and **(D)** shows the obtained pattern on the acceptor substrate flipped right side up.

Figs. 2A-D. RTP process scheme according to an embodiment of the invention, where: **(A)** shows a donor substrate with the donor pattern, **(B)** shows an acceptor substrate placed above the donor substrate, **(C)** shows the obtained pattern on the acceptor substrate; and **(D)** shows the obtained pattern on the acceptor substrate.

Figs. 3A-D. present the RTP experiment setup with 0.1mm gap between the donor substrate (bottom) and the acceptor substrate (top), where: **(A)** shows a screen-printed precursor pattern of copper formate based dispersion ink on a donor substrate before RTP process is applied (before ink decomposition), **(B)** after decomposition and transfer of metallic copper to the acceptor substrate, forming the mirror image of the precursor pattern. The pattern has amorphous borders, this is different than the result in a setup with a smaller gap, **(C)** and **(D)** copper pattern transferred to PEN according to the method of the invention.

Fig. 4. Simultaneous thermal analysis - Mass spectrometer. Solid lines: MS data for m/z numbers showing a change in intensity of the measurement. All changes were observed at 150-180°C. Dotted line: Thermal Gravimetric data, showing a 56.4% decline at 150-180°C.

Figs. 5A-G. (A) The donor pattern before (left), and after (middle) decomposition, and the transferred pattern (pure copper) on the acceptor substrate (right). SEM micrographs of: (B) copper formate particles before decomposition, (C) Porous layer of the donor after decomposition. (D)-(G) thin layers deposited on the acceptor substrate with a gap distance of 1mm, 0.6mm, 0.1mm, 0mm between acceptor and donor. All white bars represent 500nm.

Fig. 6. XRD analyses of a copper pattern on PEN preformed on the day the sample was prepared (Feb 4th, 2014) and one year later (Feb 26th, 2015), showing that only copper was detected without any oxides in both measurements, thus the sample is stable.

Figs. 7A-C. Cross section of lines showing the height profile of: (A) a dry line of copper formate after printing and drying; (B) a copper line made by decomposition of the copper precursor (MOD method) showing a line height of 3-4 μ m, (resistance 16.7 Ω); and (C) a copper line made by transfer method of the present invention, showing a line height max 230nm (resistance of 8.8 Ω). All patterned lines had a length of 23mm.

Fig. 8. Copper line height (thickness of copper line) obtained by the transfer process of the invention performed at 200°C when varying gap distances between the donor and the acceptor substrates.

Fig. 9. This graph shows the percent of copper transferred from the donor substrate to the acceptor substrate depending on the gap between the substrates. The graph shows that the bigger the gap, the less copper was transferred. The percent of transferred copper was calculated by the ratio of the mass of copper on the donor substrate and on the acceptor substrate after decomposition and transfer. The pattern transferred contains three lines, as in **Fig. 5A**.

Fig. 10. This graph shows the mass of copper transferred during RTP when heating the samples to different temperatures. The line with diamond symbols shows the mass transferred to a glass acceptor substrate, and the line with square symbols shows the average resistance of these samples, note that this line begins at 170°C as samples prepared below this temperature were non-conductive. The triangle line represents the mass transferred to a PEN acceptor substrate, this material deformed when heated to 230°C and above. All samples were positioned with a 0.1 mm gap and heated in the oven for 30 minutes.

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Figs. 11A-B. RTP preformed from and to glass substrates, using different gap sizes (w/o gap, 0.1mm, 1mm) and opposite positioning of the substrates. The two positions are illustrated: with the donor above the acceptor (**A**), so the material is transferring down (Experiments A1, A2, A3), and the acceptor above the donor (**B**) so the material is transferring up (Experiments B1, B2, B3).

Fig. 12: Various heights of donor patterns (empty bar), donor copper mass (dashed bar) and percent of copper transferred (filled bar) for patterns prepared with a 0.1 mm gap by screen printing with five screen types of different thread counts (with a thread density of 24,31,55,100 and 180 threads per cm).

Fig. 13: Resistance parameters of lines prepared with different donors heights as presented in **Fig. 12** are presented for patterns prepared with 0.1mm and w/o a gap.

Figs. 14A-B: Copper formate film with a negative pattern engraved by laser: (**A**) donor substrate before transfer process and (**B**) acceptor substrate after transfer process.

Figs. 15A-C: Copper electrode printed on a plastic substrate (PEN). Pictures were taken during a flexibility test during which the samples were taken from a flat form (not shown) to a (**A**) partial bent form, (**B**) final bent form and (**C**) the sample's resistance over 1000 bending cycles.

Figs. 16A-C. Images of screen printed copper formate lines on (**A**) aluminium foil and the glass vial wrapped with the printed lines (**B**) before and (**C**) after transfer process (RTP).

Figs. 17A-C. (**A**) Copper pattern transferred to PEN, (**B**) pattern transferred to the interior of a glass vial before and (**C**) after the transfer process.

Fig. 18. A copper pattern after transfer from an aluminum foil to a glass slide.

Figs. 19A-D: SEM micrographs of (**A**) the copper formate particles before decomposition, (**B**) copper particles left on the donor substrate, (**C**) thin layer deposited on the acceptor substrate, (**D**) thick layer deposited on the acceptor substrate.

DETAILED DESCRIPTION OF EMBODIMENTS

Experimental techniques

Methods of characterization of the printed patterns

Compositional analysis

For compositional analysis, DSC (Differential Scanning Calorimetry) and TGA (Thermal Gravimetric Analysis) were coupled with MS (Simultaneous thermal analysis-

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Mass spectrometer). Mass spectrometry measurements of the dried ink for m/z number (mass-to-charge ratio) indicate the release of various volatile by-products.

Structure and morphology characterization

Structure and morphology were acquired using high resolution scanning electron microscopy (HR-SEM, MagellanT XHR SEM).

Compositional analysis

XRD measurements were performed with D8 Advance diffractometer (Bruker AXS, Karlsruhe, Germany).

The % wt. of the metal entities transferred from the donor substrate to the acceptor substrate was measured with Inductively Coupled Plasma (ICP-OES, model Optima 3000 by Perkin Elmer).

Thickness measurements

Thickness and cross sectional height profiles of the coatings was measured with Profilometer Veeco Dektak 150.

Resistance measurements

Resistance measurements were performed with an ohmmeter (UNI-T). Resistivity was calculated using the line length and cross section area as measured by a mechanical profilometer.

Bending tests

The resistance was measured during a flexibility test in which the samples were bent from a flat form (not shown) to a bent form (**Fig. 15A** partial, **Fig. 15B** shows the final bent form). The sample was tested over 1000 bending cycles during which resistance of the lines was measured.

Adhesion tests

Adhesion between the deposited pattern and the acceptor substrate was tested by exfoliation with scotch tape (Magic™ tape, 3M). A tape is placed on the pattern and then peeled. The coating adhesion stability of the layer was observed.

Temperature stability tests

The performance evaluation of the patterns deposited on acceptor substrate was carried out by subjecting them to air during various time durations. Thereafter, the presence of oxides was measured by XRD and the resistance of the patterns was measured as above mentioned.

Materials and methods of preparation

Example 1- Obtaining pattern from copper formate nanoparticles dispersion using glass donor and glass acceptor substrates

An ink containing copper formate was prepared and printed on a donor substrate as described below. The donor was used for the RTP method to pattern copper on an acceptor substrate in the following manner:

Copper formate NPs dispersion ink preparation: Copper formate (45 wt%, Wuhan Kemi-works) in the form of particles with a median diameter of 54 μm (Eye-tech, Ankersmid), was mixed with Dipropylene glycol monomethyl ether (DPM, 47.5 wt%, purum grade, Sigma-Aldrich) and Disperbyk 180 (7.5 wt%, BYK). The crude dispersion was milled in a wet bead mill (WAB Dyno mill) for 30 minutes to obtain a dispersion containing submicron particles with an average size of 320 nm (DLS, ZetasizerNano, Malvern). HR-SEM image (**Fig. 5B**, the white bar represents 500nm scale bar) reveals that the size of NPs in the ink is in the range of 20-250nm with various morphologies. The difference between these results originates from the non-spherical morphology of the particles that is not accounted for in DLS measurements. After grinding, the excess of the dispersing agent was removed by dilution with DPM (four fold), followed by separation of the particles by centrifugation. The supernatant was discarded, leaving a concentrated dispersion. This step was preformed three times, thus lowering the amount of dispersing agent to less than 1 wt% (determined by TGA, STAR system, Mettler Toledo, not shown). This dispersion contained 21 wt% copper, and was used as ink.

Screen printing of the ink on a glass donor substrate: A polyester mesh (100 threads/cm, NBC, Ponger 2000) was patterned (*See Fig. 5A*) by conventional screen preparation process (emulsion). This screen was used for manual printing with a rubber squeegee. The lines printed to test conductivity were of the following dimensions: length: 24mm, width: 1.3mm with pads for electrodes on both ends as can be seen in **Fig. 5A**.

Post printing treatment of the donor pattern: After printing, the solvent from the ink was evaporated from the printed samples by heating on a hot plate to 70°C for 5

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minutes. All samples (unless indicated otherwise) had a pattern with dry precursor height of 8-10 μ m.

Substrate set up: An acceptor glass substrate was placed in proximity to the donor substrate. The two substrates are positioned with respect to one another at various distances (0-1mm), which, without being bound by theory, influences the amount of copper transferred (*See* Example 1.7). The height difference was maintained by using glass spacers of different thicknesses, as illustrated in **Fig. 1B** and **Fig. 2B**.

Decomposition reaction by heating: Samples were placed in a cylindrical oven in a glass cylinder, allowing the reaction to take place under an inert environment. Prior to heating, nitrogen gas was flowed (10 L/min) for 5 minutes to ensure the washout of residual oxygen. The cylinder with the samples was placed in the pre-heated oven to a temperature of 100-300°C for 30 minutes, while nitrogen gas flow was set to the range of 2 L/min. Thirty minutes were found sufficient for all processes performed at temperatures above 170°C as the reaction took place upon reaching a sufficient temperature for permitting decomposition. After the heating, the glass cylinder was exerted from the oven and allowed to cool to room temperature while nitrogen flow was set to 6 L/min.

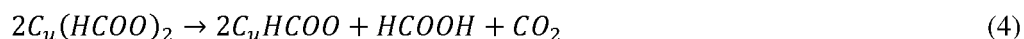
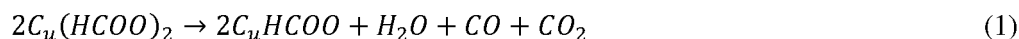
Fig. 3 shows a setup of the printing scheme according to one embodiment of the invention with a 0.1 mm gap between the donor substrate (bottom) and the acceptor substrate (top). On the donor substrate is a pattern of copper formate printed by screen printing of said dispersion ink (**Fig. 3A**, before decomposition). Upon thermally decomposing the printed patterns of copper formate under an inert environment (e.g., nitrogen or argon), in proximity to a parallel acceptor substrate, the pattern transfers to the acceptor substrate. This produces a pattern with the mirror image of the first pattern printed on the donor substrate (**Fig. 3B**, after decomposition). It was found that the obtained pattern is composed of pure copper and is highly conductive. **Figs. 3C** and **3D** presents a plastic acceptor substrate (PEN) to which a copper pattern was transferred by the same method. This method enabled fabrication of copper patterns with 50% bulk copper conductivity.

In order to elucidate the mechanism of the copper pattern formation, the decomposition process of the copper formate ink was investigated by DSC and TGA coupled with MS (Simultaneous thermal analysis - Mass spectrometer, *See* **Fig. 4**),

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since the process occurs upon heating. It was found that the decomposition takes place at the range of 155-188°C with a DSC peak at 175°C. Mass spectrometry measurements of the dried ink for m/z number (mass-to-charge ratio) indicate the release of various volatile by-products. The main detected m/z numbers are 44, 18, 16, 29, 12, 17, which correlate well with CO₂, H₂O, O, CHO and C. The m/z numbers 16, 29, 12 and 17 are in agreement with the known MS data of formic acid (NIST Mass spectrometry data center). CO was not measured as it has the same m/z number as nitrogen which was used as a carrier gas. Since Karl Fischer titration tests indicate that the ink does not contain water, the detected water must originate from the decomposition process.

Without wishing to be bound by theory, the decomposition process of copper formate to copper metal involves the following steps:



The detection of water by MS indicates the occurrence of Equation (1). The absence of copper (I) formate in the MS results is probably due to the fast reduction to Cu⁰ according to Equation (2), yet it is believed it should be formed since Equation (1) is the only possibility to form water.

The following examples show results of some embodiments of the present disclosure. The parameters are as in the general case above unless indicated otherwise.

Obtaining a Cu pattern under RTP conditions using various gap sizes between a glass donor substrate and a glass acceptor substrate

Example 1.1: 0.2mm gap

A glass donor substrate was placed in proximity to a glass acceptor substrate with at a distance of 0.2mm between them. The two substrates were heated to a temperature of 185°C for 30min in a nitrogen environment resulting in the decomposition of the copper formate and the transfer of the pattern to the acceptor

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substrate (as shown in **Fig. 5A**). The transferred pattern is the mirror pattern of the donor pattern. XRD analysis revealed that the obtained pattern contains only copper (**Fig. 6**) without any copper oxides. The obtained resistance of one of the lines was 4.9Ω and the cross section area was measured to be $154.38\mu m^2$. The resistivity was calculated to be $3.15 \cdot 10^{-8}\Omega m$, only 1.83 times higher than the resistivity of bulk copper. This result indicates that the process can be used as an indirect method for patterning pure copper patterns with excellent resistivity.

Example 1.2: 0.1 mm gap

A glass donor substrate was placed in proximity to a glass acceptor substrate with at a distance of 0.1mm between them. The two substrates were heated to a temperature of $200^\circ C$ for 30min in a nitrogen environment resulting in the decomposition of the copper formate and the transfer of the pattern to the acceptor substrate. The transferred pattern is the mirror pattern of the donor pattern. The obtained resistance of one of the lines was 3.7Ω and the cross section area was measured to be $213.78\mu m^2$. Resistivity was calculated to be $3.29 \cdot 10^{-8}\Omega m$, 1.96 times higher than the resistivity of bulk copper. This result indicates that the process can be used as an indirect method for patterning pure copper patterns with excellent resistivity.

Example 1.3: RTP with 0.2mm gap compared to samples prepared without a gap (without a spacer, 0mm gap)

In a similar setup to Example 1.1, two samples were tested, one with a distance between substrates of 0.2mm, the second without spacers (0mm). The obtained resistance with a spacer was $\sim 3.2\Omega$, while without a spacer the resistance was $\sim 1.96\Omega$. These results indicate that without a spacer lines with a lower resistance are obtained. In addition these results indicate that the process can be performed with contact between the two substrates, or with a gap therebetween.

Example 1.4: Stability of the obtained copper patterns under air over duration of time

The patterns formed by the method of the invention under RTP conditions were found by XRD to be stable in air for long time periods. A sample prepared similar to Example 1.1 with a gap of 0.1mm was measured twice by XRD, on the day it was prepared and over a year later. The XRD data displayed in **Fig. 6** indicate that even after

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one year, the pattern contains 100% copper, with no oxides. This unique and surprising stability is attributed to the dense packing of the obtained patterns. The results exhibit that the pattern obtained by the method of the present disclosure is distinguished from other methods of printing patterns with copper nanoparticle ink or other precursors printing techniques.

Example 1.5: Height of patterns obtained by the process of the invention under RTP conditions in comparison to MOD method

Donor patterns with a dry ink height of 8-10 μ m (displayed in **Fig. 7A**) were used as a pattern for MOD printing method and for the method of the present invention in order to compare the final height of the obtained copper pattern. The MOD method was performed by heating the sample under nitrogen when it was facing up (without use of a second substrate). After decomposition at 185°C for 30min the pattern had a height of 3-4 μ m (displayed in **Fig. 7B**). A sample prepared similar to Example 1.1 with a gap of 0.1mm at the same heating parameters resulted in an accepted pattern with a maximum height of 230nm (displayed in **Fig. 7C**).

Without wishing to be bound by theory, the difference in pattern height is because in the method of the invention, the metal accumulates on the acceptor substrate, rather than being printed as part of the ink as in MOD. The RTP results in a pattern that has a more continuous morphology as compared to that obtained by MOD (very porous), and thus this pattern is more stable to oxidation and has a lower resistivity. Furthermore, unlike direct printing, in which the amount of ink printed is fixed according to the method of printing, the transferred amount depends on various parameters such as gap distance and heating profile.

Example 1.6: Height of patterns obtained as a function of gap size between the donor and acceptor substrates

The effect of the distance between the two substrates on the transferred copper thickness is presented in **Fig. 8**. Six samples with gap distances between the donor and the acceptor substrates of 0, 0.1, 0.2, 0.4, 0.6, 1mm were prepared similar to Example 1.1 at 200°C and their height was measured by profilometer. It was found that as a smaller gap was used (so the distance between the substrates decreases), a thicker

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copper layer is transferred to the acceptor substrate, while the thickest layer was obtained for samples prepared without a gap.

Example 1.7: Mass of copper transferred as a function of gap size

The effect of the distance between the two substrates on the amount (mass) of transferred copper is presented in **Fig. 9**. Four samples with gap distances between the donor and the acceptor substrates with gap distances of 0, 0.1, 0.4, 1mm were prepared similar to Example 1.1 at 200°C, and the mass of the copper on the donor and acceptor substrates was measured. This was carried out by oxidizing the copper patterns with nitric acid, dilution to a known volume with TDW (triple distilled water) and measuring the copper concentration in the solution with Inductively Coupled Plasma (ICP-OES). The percent of transferred copper was calculated by the ratio of the mass of copper on the donor substrate and on the acceptor substrate after decomposition and transfer. The graph shows the percent of copper transferred from the donor substrate to the acceptor substrate depends on the gap between the substrates. This experiment shows that the smaller the gap, the less copper was transferred. This correlates well with the findings in Example 1.6 as the amount of copper transferred affects the pattern height.

Example 1.8: Mass of copper transferred as a function of oven temperature

The effect of the oven temperature on the amount (mass) of transferred copper is presented in **Fig. 10**. This graph shows the mass of copper transferred during RTP when heating the samples to different temperatures. All samples were positioned with 0.1mm gap and heated in the oven for 30 minutes. In every temperature two samples were tested, one with a glass acceptor substrate, and one with a plastic (PEN) acceptor substrate. The line with diamond symbols shows the mass transferred to the acceptor substrate, and the line with square symbols shows the average resistance of the three lines in each sample, note that this line begins at 170°C as samples prepared below this temperature were non-conductive. The line with triangle symbols represents the mass transferred to a PEN acceptor substrate, this material deformed when heated to 230°C and above. These results show that more copper transfers during the process of the invention when performing the decomposition in an oven with a higher temperature. The mass of copper on the acceptor substrates was measured with ICP-OES as described in Example 1.7.

Example 1.9: Positioning of the samples using differing gaps

The method of the invention was performed similar to Example 1.1 at 200°C, with samples in different setups of gap sizes (w/o gap, 0.1mm, 1mm) and positioning of the substrates. The two positions are illustrated in **Fig. 11**: with the donor above the acceptor (**Fig. 11A**), so the material is transferring down (Experiments A1, A2, A3), and the acceptor above the donor (**Fig. 11B**) so the material is transferring up (Experiments B1, B2, B3). It is appreciated that samples with opposite positioning are very similar and that samples prepared with 1mm gap have fuzzy borders, which are unlike the sharp edges of samples prepared with 0.1mm and 1mm gaps. In general, it was found that the resolution depends on the gap distance; sharper edges were viewed when smaller gaps were used.

Without being bound by theory, it is expected that resolution depends on the process for printing donors, thus ranging from hundreds of micron patterns down to nanometric dimensions.

Example 1.10: The morphology of copper transferred as a function of gap size

Fig. 5A presents the printed patterns before decomposition and the donor and transferred pattern obtained after decomposition. The donor pattern of printed and dried ink before transfer (left) is characterized by a pale blue color typical for copper formate. HR-SEM image (**Fig. 5B**) reveals that the size of NPs in the ink is in the range of 20-250nm with various morphologies. After decomposition, this donor pattern turns to a brown colour with a porous morphology (**Fig. 5A** middle and **Fig. 5C**) composed of copper NPs with a similar size range. The RTP transferred pattern was evaluated for four samples prepared similar to Example 1.1 at 200°C, with various gap distances between the donor substrate and the acceptor substrate (1mm, 0.6mm, 0.1mm, 0mm). According to X-ray diffraction (XRD) analysis, the transferred copper layers were found to be pure crystalline fcc copper (e.g. **Fig. 6**). The transferred patterns had a shiny cupric colour while their morphology was strongly dependent on the gap between donor and acceptor. At a large gap (1mm), the obtained layer is non-continuous, and as displayed in **Fig. 5D**, it consists of small islands (diameter of 10-20nm). A more continuous and dense film is obtained as the gap decreases as shown for gaps of 0.6mm and 0.1mm (**Fig. 5E** and **Fig. 5F**). When observing the morphology of a structure made without a gap, (a distance of 0mm, **Fig. 5G**), the copper transferred layer is continuous.

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These results show another advantage of the suggested process of the invention, the ability to obtain a continuous and dense layer of the transferred material. SEM images were obtained on a MagellanT XHR SEM.

Example 1.11: Obtaining a pattern under fast heating and transfer

The method and therefore the decomposition and transfer may be much shorter than 30 minutes. For example, a pattern of copper formate particles was heated to 260°C under nitrogen for 30 seconds by placing the sample on a preheated hot plate, which led to the formation of a highly conductive copper pattern on the acceptor substrate.

In a different experiment, the same cylinder oven as in Example 1.1 was used, but it was preheated to 600°C, the samples were placed in a glass cylinder with an attached thermocouple, and then inserted to the oven. When the temperature in the cylinder reached 200°C (after 180 seconds) the cylinder was removed from the oven. The resistance of lines obtained with RTP setup of 0.1mm gap and without a gap (0mm) were measured and found to be in the range of 4-20 Ω , thus showing that the process can be performed in shorter time frames than 30 minutes.

Example 1.12: Obtaining a pattern at low temperatures

The method and therefore the decomposition and transfer may be performed with temperatures lower than 170°C. When heating at lower temperatures, the copper formate only partially decomposes after 30 minutes, so a longer heating time is required.

A similar method to Example 1.1 was carried out at 161°C for 60 minutes (instead of 30min) resulting in resistance of 3.03 $\pm$ 0.20 Ω for lines transferred to glass without a spacer, and resistance of 6.8-111.3 Ω for lines transferred to PEN with a 0.1mm gap.

The method was also performed at 132°C and 146°C for 90 minutes after which not all of the copper formate decomposed but a small amount of copper was seen on the acceptor substrates. The copper layer transferred was pale and these samples were not conductive, but this experiment shows that the decomposition and transfer occurs at lower temperatures, but the kinetics are very slow.

Example 1.13: Printing under RTP conditions twice to the same acceptor

The process of the invention was performed similar to Example 1.1 at 200°C, with samples in different setups of gap sizes (w/o gap, 0.1mm, 1mm) and positioning of the substrates.

The process was performed similar to Example 1.1 at 200°C twice to the same acceptor substrate. The double transfer resulted in lines with more copper and the lowering of line resistance. After one cycle of the process, the resistance of the samples was measured, after which, the sample was positioned and aligned with a new donor substrate (with unreacted copper formate) and heated to enable a second layer of copper. Resistance fell from $7.7 \pm 1.5 \Omega$ to $3.9 \pm 0.3 \Omega$ after the second process cycle (based on six measurements).

Example 1.14: Printing under RTP conditions using anhydrous copper formate and hydrous copper format

A dispersion ink of hydrous copper formate was prepared by a similar procedure to that described in Example 1. Donor patterns with this ink and with the anhydrous copper format were prepared and used for printing under RTP conditions (as in Example 1.1) with 0mm gap and w/o a gap. Patterns with both inks transferred as a result of applying the process. The percent of copper transferred was found (as in Example 1.7) to be 16.07% w/o a gap, and 9.91% with a 0.1mm gap, when using the copper formate hydrous ink, and 20.21% w/o gap and 12.10% with 0.1 mm gap when using the copper formate anhydrous ink. This shows that both forms of copper formate can be used as precursor material for printing under RTP conditions. In addition, it seems that using copper formate anhydrous leads to slightly more copper transfer.

Example 1.15: Printing under RTP conditions using donor patterns with varying heights

Donor patterns with varying pattern heights and donor material mass were prepared by screen printing with screens of different thread counts. When using screens with denser weaving (more threads per cm or inch) less ink is applied. Five types of screens were used, with a thread density of 24,31,55,100 and 180 threads per cm. All screens had the same pattern as in Example 1.1, so lines of the same shape, but with varying thickness were printed. Printing under RTP conditions was performed with

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these donor patterns as in Example 1.1 at 190°C. The height of the patterns, mass of copper (as measured by ICP) and the percent of copper transferred (for patterns prepared with a 0.1mm gap) as shown in **Fig. 12**. In general, as a screen with a higher thread count was used, a thinner pattern with less precursor was printed.

Resistance parameters of lines prepared with the different donors are presented in **Fig. 13** for patterns prepared with 0.1mm and w/o gap. When looking at the resistance of patterns prepared with 0.1mm gap, as a screen with a higher thread count (and less precursor on the donor) was used the resistance decreases (24 to 55 [threads/cm] screen), but when using a denser screen, the resistance increases (55 to 180 [threads/cm] screen). Samples prepared without a gap show the opposite behavior. Without being bound by theory, this may be a result of the transfer mechanism.

Example 1.16: Printing under RTP conditions using copper formate ink that was not washed from the dispersing agent

A dispersion of copper formate was prepared in a similar way as in Example 1, but without the washing step after the grinding. After grinding the dispersion was centrifuged in order to separate some of the DPM and so obtain an ink with a high solid percentage suitable for screen printing. This ink was printed and used for RTP in accordance with Example 1 with 0.1mm gap. The RTP lead to the formation of conductive copper patterns on the acceptor glass substrate with resistance values of $1.51 \pm 0.02 \Omega$, and the percent of copper transferred was 62.92% (as in Example 1.7).

Example 1.17: Transfer of copper from a copper formate pattern prepared by inkjet printing, using glass donor and acceptor substrates

A dispersion of copper formate was prepared similarly to Example 1.1, but with 3 hours grinding time, thus obtaining a finer dispersion that was filtered through a 1.2µm glass fiber syringe filter (Pall). The dispersion was formulated to an inkjet ink by addition of DPM (50 wt%) and a wetting agent (BYK 333, less than 0.1 wt%). The ink was inkjet printed on glass to form a pattern (three lines of 1.3X25 mm). An RTP process was performed in a similar setup to Example 1.1 at 180°C with 0.1mm and w/o gap. The RTP process lead to the formation of conductive copper patterns on the acceptor glass substrate with resistance of $1.30 \pm 0.03 \Omega$ and $10.20 \pm 6.08 \Omega$, respectively. Lines prepared with 0.1mm gap were characterized. The resistivity was $1.49 \cdot 10^{-7} \Omega \text{m}$,

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8.6 times higher than the resistivity of bulk copper and the percent of copper transferred was found to be 84%. These results demonstrate that the donor patterns can be prepared by ink-jet printing in addition to screen printing. In addition these results demonstrate the use of a non-washed ink (compared to the ink used in Example 1.1) resulting in the transfer of conducting patterns.

Example 1.18: Glass donor substrate coated with copper formate precursor ink by K-bar coater

A copper formate particles ink was used to make a thin continuous film of the precursor on a glass donor substrate with a K-bar coater #3. After coating, the solvent was evaporated by heating to 70°C for 5 min. using the RTP process at 200°C lead to the formation of conductive copper film on acceptor glass substrates with a sheet resistance of $1.8\Omega/\square$ (ohm per square) with a 0.1mm spacer, and $4\Omega/\square$ w/o a spacer.

Example 1.19: Copper formate ink with laser-engraved pattern

A copper formate particles ink was used to make a thin film of the metal salt on a glass donor substrate with a K-bar coater #3. After coating, the solvent was evaporated by heating to 70°C for 5min. A laser beam printer/engraver (Universal Laser Systems) was used to print a pattern on the dry film, resulting mainly in the removal of the material, thus leaving a copper formate film with a pattern where the graphics do not contain copper formate, as shown in **Fig. 14A**. This pattern was transferred to a second glass slide by the same transfer process described in Example 1.1. The resulting copper with the engraved pattern film on the acceptor substrate after the transfer process is shown in **Fig. 14B**. The pattern engraved by the laser is “burned out”, so it does not contain copper formate. As appreciated, copper appears only where the laser engraver did not decompose the copper formate prior to the transfer process.

Example 1.20: Obtaining a pattern under argon atmosphere

The effect of the inert gas used throughout the process was examined by comparing samples prepared under nitrogen and argon. Samples with copper formate were prepared and positioned with a 0.1mm gap and w/o a gap from glass and PEN acceptor substrates (a sum of 4 samples), decomposition was performed as in Example 1 with an oven temperature of 200°C, and an argon/nitrogen flow of 2 L/min. all samples resulted in the transfer of copper to the acceptor substrate to form conductive

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lines with low resistance. Samples transferred to glass and PEN with 0.1mm gap under nitrogen had an average resistance of $11.46 \pm 4.78 \Omega$ and $11.83 \pm 5.27 \Omega$, respectively. The same setup under argon resulted in average resistance of $22.7 \pm 18.06 \Omega$ and $9.3 \pm 3.75 \Omega$, respectively. In addition, the percent of copper transferred was found (as in Example 1.7) to be 22.15% to glass and 23.46% to PEN under nitrogen, and 20.63% to glass and 23.27% to PEN under argon. Thus, the transfer method of the invention can be performed successfully both under nitrogen and under argon.

Example 1.21: Obtaining a pattern with a donor pattern prepared with a water-salt solution ink

An ink was prepared by dissolving copper formate (12.5 wt%) in triple distilled water followed by filtration through a $0.45 \mu\text{m}$ syringe filter. The ink was used as is and a line was drawn on a glass substrate and was dried at 70°C on a hot-plate. The pattern was used in a RTP setup similar to Example 1.1, resulting in a conductive copper pattern on the acceptor substrate.

Example 1.22: Obtaining a pattern using different metal precursors

Various precursors were tested with powder of the precursor by placing a small amount of the salt on a glass slide, and heating it with an acceptor slide above it (1mm high so the slide will not be in direct contact with the powder) in a nitrogen environment (4 L/min) as follows:

- Copper acetate was heated to 320°C resulting in transfer of copper to the acceptor substrate, the transfer was found to be less effective compared to copper formate in means of localization of the transfer and the obtained conductivity.
- Copper acetylacetonate was heated to 500°C resulting in transfer of copper to the acceptor substrate.
- Palladium acetylacetonate was heated to 500°C resulting in transfer of palladium to the acceptor substrate.
- Iron acetylacetonate was heated to 500°C resulting in transfer of a small amount of Iron to the acceptor substrate.
- Tin chloride anhydrous, Tin chloride 2 hydrate, were heated to 450°C for 30 minutes resulting in transfer of tin to the acceptor substrate.

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- Tin (II) athylhexanoat were heated to 450°C for 30 minutes resulting in transfer of tin to the acceptor substrate.
- Indium acetate was heated to 450°C resulting in transfer to the acceptor substrate, resulting it electrical conductivity on the acceptor substrate.

Example 2: Obtaining a pattern with a glass donor substrate and a plastic acceptor substrate (Kapton, PET and PEN- Polyethylene Naphthalate)

Example 2.1: Glass donor substrate and Kapton acceptor substrate under nitrogen

A copper formate pattern on glass as described in Example 1.1 was used as a donor pattern. Kapton (polyimide) was used as the acceptor substrate. The Kapton was placed on a metal sheet to efficiently transfer heat to the substrate, and above it, the donor pattern was placed with a gap of 0.1 mm. The sample was heated in a nitrogen environment to a temperature of 185°C for 30min, after which the pattern was transferred to the Kapton substrate. Three lines were found to have a low average resistance of $3.73 \pm 0.55 \Omega$.

Example 2.2: Glass donor substrate and PEN acceptor substrate under nitrogen and argon

A copper formate pattern on glass as described in Example 1.1 was used as a donor pattern. PEN (polyethylene naphthalate) was used as the acceptor substrate. Results for this experiment are indicated in Example 1.18 for nitrogen and argon environments.

Example 2.3: Adhesivity tests of the patterns obtained

Adherent stability between the copper pattern and the plastic substrates was tested by exfoliation with scotch tape (Magic™ tape, 3M). The tape was applied to patterns on PEN and than peeled away, the copper transferred to PEN was found to be stable and did not peel with the tape.

Example 2.4: Transfer of patterns from rigid to flexible substrates and from flexible to rigid substrates

A copper formate particles ink as in Example 1.1 was used to make a thin film of the precursor on a glass donor substrate with a K-bar coater #3. After applying the ink, the solvent was evaporated by heating to 70°C for 5 min. PEN and Kapton were

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used as acceptor substrates, and were placed on a metal sheet to efficiently transfer heat to these substrates. The substrates were placed in proximity to the printed pattern (0.1mm) by using glass spacers on either side of the pattern. The substrates were heated in a nitrogen environment to a temperature of 185°C for 30 min, after which a thin copper film was found on the PEN and Kapton films. The films were found to have a sheet resistance of $1\Omega/\square$ (ohm per square) and $0.5\Omega/\square$ (ohm per square) on PEN and Kapton, respectively. These examples demonstrate that the transfer method of the invention enables to transfer pattern from rigid to flexible substrates. The vice versa option, i.e., the transfer from a flexible substrate to a rigid substrate or from flexible to flexible, is possible as well.

Example 2.5: Flexibility of copper electrodes prepared by transfer process on PEN substrate

Copper electrodes were printed on a plastic substrate (PEN Q83, 125 μ m) as in Example 1.1. The resistance was measured during a flexibility test in which the samples were taken from a flat form (not shown) to a bent form (**Fig. 15A** partial, **Fig. 15B** shows the final bent form). The sample was tested over 1000 bending cycles with as little as a 50% increase in resistance as shown in **Fig. 15C**. These results indicate that the process can be used for obtaining flexible copper patterns.

Example 2.6: Transfer process on PET acceptor substrate at low temperature

Samples prepared similar to Example 1.1 at 120° for 90 minutes, with different setups of gap sizes (w/o gap, 0.1mm) and a PET acceptor substrate. During the heating, not all of the copper formate decomposed, but after removing the sample from the oven a small amount of copper was seen on the acceptor substrates. The copper layer transferred was pale and these samples were not conductive. This experiment shows that the decomposition and transfer can occur at lower temperatures, and a PET acceptor substrate can be used.

Example 3: Obtaining a pattern with aluminium foil as the donor substrate

Example 3.1: Aluminium donor substrate and glass acceptor substrate

A copper formate particles ink was used to print a copper formate pattern on aluminium foil as the donor substrate (**Fig. 16A**). This foil was then wrapped over a curved substrate: a glass vial (**Fig. 16B**). The wrapped vial was heated under nitrogen

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atmosphere for 30min at 200°C. The mirror image of the printed pattern was transferred to the glass vial as pure conductive copper. (**Fig. 16C**).

Without being bound by theory, it is expected that the mechanism and the chemical process occurring during decomposition of the metal precursor should not be different when using the method on a 2D substrate or on a 3D object.

Example 3.2: Obtaining patterns on curved surfaces

A copper formate particles ink was used to print a copper formate pattern on aluminium foil as the donor substrate (**Fig. 17A**). This foil was then placed adjacent to the inside surface of a glass vial (**Fig. 17B**). The vial was heated under nitrogen atmosphere for 30min at 200°C. The mirror image of the printed pattern was transferred to the interior glass vial as pure conductive copper (**Fig. 17C**). These results indicate that the process can be used for obtaining copper patterns on curved surfaces, even in places that conventional printing methods cannot be used.

Example 3.3: Obtaining a pattern on a needle

A copper formate particles ink was used to print a copper formate pattern on aluminium foil (as the donor substrate). This foil was wrapped around a glass needle. After decomposition, a thin conducting layer was formed on the needle.

Example 3.4: Single step pattern printing on highly curved substrate

A copper formate particles ink was used to print a copper formate pattern on aluminium foil (as the donor substrate). The pattern was wrapped around a microscope slide and heated under nitrogen for 30 minutes to a final temperature of 195°C. After heating the pattern was transferred to the slide, making continuous conductive lines that pass four 90° angled corners with a resistance of $\sim 83\Omega$. Therefore, this transfer method was found to be a powerful tool to print a conductive pattern in a single step on corners and highly curved substrates.

Example 3.5: Transferring a copper pattern from aluminium foil to both sides of a glass slide

In a similar setup to Example 3.4, an aluminium foil sheet was coated with the ink, dried, and a 5x1 cm ribbon was cut from the sheet. The ribbon was wrapped around a glass slide and heated to permit transfer of the pattern. As shown in **Fig. 18**, the

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pattern was deposited on both sides of the slide, starting from one side to the edge, to the other side and back to the first side. High conductivity (resistance of $\sim 10\Omega$) was measured from end to end even through the two edges.

Example 3.6: Aluminium foil donor substrate and various acceptor substrates for patterning jewellery

The ink described in Example 1.1 was used to print a pattern on aluminium foil. The pattern was wrapped around glass beads, leaded crystal balls, jade stones and a blue lace agent stones. Performing the same transfer process as described above led to the formation of copper pattern on the mentioned acceptor substrates. This example shows that the process of the invention can be used for jewellery making.

Example 4: Transfer of conductive transparent materials

Example 4.1 Transfer of a transparent metal oxide conductive layer

Indium acetate was placed on a substrate as the donor pattern. Then, a second glass slide was placed on top (with a spacer in between). After heating to 450°C for 30 minutes under nitrogen, a transparent conductive layer was formed on the acceptor glass.

Example 4.2: Transfer of a metal mesh

A mesh pattern of copper formate was formed as described previously (Layani et al. Journal of Materials Chemistry 21.39 (2011): 15378-15382). Then, the metal mesh pattern was used as a donor pattern to form a conductive copper mesh pattern on the acceptor substrate. It was found that a metallic mesh pattern is formed on the donor substrate and may be used as a transparent conductive layer.

CLAIMS:

1. A method for indirectly forming a metallic pattern on a surface region of a substrate, the method comprising forming a mirror image of said metallic pattern on a surface region of a first substrate and causing transfer of said pattern to a surface region of a second substrate under conditions of reactive transfer printing (RTP), wherein the mirror image is formed of a metal precursor material.
2. The method according to claim 1, for forming a metallic pattern on a substrate, the method comprising applying reactive transfer printing (RTP) conditions to a pair of face-to-face oriented solid surfaces, one of said solid surfaces having on a surface region thereof a pattern of a metal precursor material, whereby a metallic mirror image of said pattern is formed on the other of said solid surfaces upon application of the RTP conditions.
3. The method according to claim 1 or 2, for fabricating a metallic pattern on a surface region of a substrate, the method comprising:

bringing into close proximity or contact a surface region of a first substrate with a surface region of a second substrate, wherein the surface region of the first substrate having a pattern thereon of at least one metal precursor material,

the method being carried out under reactive transfer printing (RTP) conditions, to allow decomposition of the at least one metal precursor material in the pattern and transfer of the decomposed at least one metal precursor material to a surface region of the second substrate, whereby a metallic pattern is formed on the second substrate.
4. The method according to claim 3, the method comprising:
 - a) forming the pattern of at least one metal precursor material on a surface region of the first substrate;
 - b) bringing into close proximity or contact the surface region of the first substrate having a pattern thereon with a surface region of the second substrate;
 - c) applying reactive transfer printing (RTP) conditions, to thereby allow decomposition of the at least one metal precursor material in the pattern and transfer of the decomposed at least one metal precursor material to a surface region of the second substrate, whereby a metallic pattern is formed on the second substrate.

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5. The method according to claim 3 or 4, the method further comprising obtaining an ink formulation comprising at least one metal precursor material; and forming the pattern of at least one metal precursor material on a surface region of the first substrate.
6. The method according to claim 5, wherein the thickness of the pattern of at least one metal precursor material on a surface region of the first substrate is between 0.01 μ m to 1mm.
7. The method according to any one of claims 3 to 6, the method further comprising pretreating the first substrate or second substrate prior to applying RTP conditions.
8. The method according to claim 3, wherein decomposing is achieved by thermal heating, laser heating, microwave heating, electrical voltage heating, or heating by exposure to light.
9. The method according to claim 8, wherein said decomposition is thermal decomposition.
10. The method according to any one of claims 3 to 9, wherein decomposing is achieved by photonic curing, UV radiation, IR radiation or by plasma treatment.
11. The method according to any one of claims 3 to 9, wherein decomposing is achieved by heating under air, nitrogen, argon or a non-oxidizing atmosphere.
12. The method according to claim 11, wherein decomposing is achieved by heating under a non-oxidizing atmosphere.
13. The method according to claim 12, wherein said non-oxidizing atmosphere is nitrogen or argon.
14. The method according to any one of claims 1 to 13, wherein reactive transfer printing (RTP) conditions are applied for a time and at a temperature sufficient to cause decomposition of the metal precursor.
15. The method according to claim 14, wherein said temperature is between 20°C to 300°C.
16. The method according to claim 14, wherein said temperature is between 150°C to 250°C.
17. The method according to claim 14, wherein said temperature is at most 200°C.
18. The method according to any one of claims 1 to 17, wherein the decomposition step is carried out at atmospheric pressure.

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19. The method according to any one of claims 1 to 18, wherein said first substrate and second substrate are each of a different material.
20. The method according to any one of claims 1 to 18, wherein said first substrate and second substrate are composed of the same material.
21. The method according to any one of claims 1 to 19, wherein said first substrate or second substrate is a flexible substrate or a rigid substrate, capable of withstanding the reactive transfer printing conditions (RTP).
22. The method according to any one of claims 1 to 21, wherein said substrate is of a material selected from plastic, fabric, composite material, laminates, glass, metal, alloy, metal oxide, semiconductor, ceramic, quartz, silicon, germanium, ITO, FTO and TiO_2 .
23. The method according to claim 22, wherein said first substrate or second substrate is of a material selected from glass, plastic, silicon and metal.
24. The method according to claim 22, wherein said plastic is a heat-resistant plastic.
25. The method according to any one of claims 1 to 24, wherein said at least one metal precursor material is in the form of a metal source selected from metal-organic complex, metal-organic salt, metal salt, metal complex particles, metal salt particles and mixtures thereof.
26. The method according to claim 25, wherein said at least one metal precursor material is in a salt form or complex form of an element selected from a transition metal, a post-transition metal and a metalloid.
27. The method according to claim 26, wherein said element is selected from Sc, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, Y, Zr, Nb, Tc, Ru, Mo, Rh, W, Au, Pt, Pd, Ag, Mn, Co, Cd, Hf, Ta, Re, Os, Al, Sn, In, Ga and Ir.
28. The method according to claim 27, wherein said element is selected from Cu, Ni, Ag, Au, Pt, Pd, Al, Fe, Co, Ti, Zn, In, Sn and Ga.
29. The method according to claim 28, wherein said element is selected from Cu, Ni and Ag.
30. The method according to claim 29, wherein said element is selected from Ag and Cu.
31. The method according to claim 30, wherein said element is Cu.

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32. The method according to any one of claims 1 to 31, wherein said metal precursor comprises an inorganic anion or an organic anion.

33. The method according to claim 32, wherein said inorganic anion is selected from HO^- , F^- , Cl^- , Br^- , I^- , NO_2^- , NO_3^- , ClO_4^- , SO_4^{-2} , SO_3^- , PO_4^- and CO_3^{-2} .

34. The method according to claim 32, wherein said organic anion is selected from formate (HCOO^-), acetate (CH_3COO^-), citrate ($\text{C}_3\text{H}_5\text{O}(\text{COO})_3^{-3}$), acetylacetonate, lactate ($\text{CH}_3\text{CH}(\text{OH})\text{COO}^-$), oxalate ($(\text{COO})_2^{-2}$), carboxylates and any derivative thereof.

35. The method according to claim 1, wherein the metal precursor is in the form of a salt or complex of copper.

36. The method according to claim 35, wherein the copper metal salt or complex is selected from copper formate, copper acetate, , copper acetylacetonate, copper oxalate, copper malonate, copper maleate, copper fumarate, copper squarate, copper mellitate, and mixtures thereof.

37. The method according to claim 36, wherein the copper metal salt or complex is copper formate.

38. The method according to claim 1, wherein the metal precursor is in the form of a salt or complex of palladium.

39. The method according to claim 38, wherein the palladium metal salt or complex is selected from palladium acetylacetonate, palladium acetate, palladium citrate, and mixtures thereof.

40. The method according to claim 1, wherein the metal precursor is in the form of a salt or complex of tin.

41. The method according to claim 40, wherein the tin metal salt or complex is selected from tin chloride and tin ethylhexanoate.

42. The method according to claim 1, wherein the metal precursor is in the form of a salt or complex of silver.

43. The method according to claim 42, wherein the silver metal salt is selected from silver oxalate, silver lactate, silver formate, silver octanoate and mixtures thereof.

44. The method according to claim 1, wherein the metal precursor is in the form of a salt or complex selected from indium acetate, iron acetate, iron acetylacetonate; gallium acetylacetonate, gallium nitrate, aluminum stearate; silver nitrate, dimethylzinc,

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diethylzinc, tin acetylacetonate, tin acetate; lead acetate, lead acetylacetonate, and lead nitrate.

45. The method according to any one of claims 1 to 44, wherein the metal precursor is selected to be convertible into a metal atom by a decomposition process.

46. The method according to any one of claims 1 to 44, wherein said metal precursor is in liquid form or in powder form.

47. The method according to any one of claims 1 to 44, wherein said metal precursor is formulated as dispersion or solution in a liquid medium.

48. The method according to claim 47, wherein said liquid medium is an aqueous medium or organic medium.

49. The method according to claim 48, wherein said organic medium is selected from glycol ether, alcohol, acetate and mixtures thereof.

50. The method according to claim 49, wherein said organic medium comprises glycol ether.

51. The method according to claim 47, wherein said metal precursor formulation further comprises a material selected from a solvent, a stabilizing agent, a surfactant, a binder, a humectant and a wetting agent, and mixtures thereof.

52. The method according to claim 51, wherein the stabilizing agent is selected from a polyelectrolyte, a polymeric material, a cationic surfactant, an anionic surfactant, a non-ionic surfactant, a zwitterionic surfactant and a cationic polymer.

53. The method according to claim 1, wherein said metal precursor being in the form of metal salt nanoparticles or sub-micron particles of copper formate dispersed in glycol ether, and further comprising a stabilizer being a functionalized polymer.

54. The method according to claim 1, further comprising a step of sintering the metallic pattern.

55. The method according to claim 1, wherein the first substrate and said second substrate are placed at a distance of between 0 and 3mm.

56. The method according to claim 1, wherein the pattern or object obtained is electrically conductive.

57. The method according to claim 1, wherein the pattern or object obtained is transparent.

58. The method according to claim 1, wherein the conductivity of the metallic pattern is above 70% of the bulk conductivity of the metal.

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- 59.** The method according to claim 1, wherein the conductivity of the metallic pattern is above 50% of the bulk conductivity of the metal.
- 60.** The method according to claim 1, wherein the conductivity of the metallic pattern is above 33% of the bulk conductivity of the metal.
- 61.** The method according to claim 1, wherein the conductivity of the metallic pattern is above 10% of the bulk conductivity of the metal.
- 62.** The method according to claim 1, wherein the conductivity of the metallic pattern is above 1% of the bulk conductivity of the metal.
- 63.** The method according to claim 1, wherein the resistivity of the metallic pattern is in the range of $1.0 \cdot 10^{-8} \Omega\text{m}$ to $2.0 \cdot 10^{-6} \Omega\text{m}$.
- 64.** The method according to claim 1, wherein the resistivity of the metallic pattern is in the range of $1.7 \cdot 10^{-8} \Omega\text{m}$ to $1.0 \cdot 10^{-6} \Omega\text{m}$.
- 65.** A method of converting a patterned metal precursor material into a metallic pattern, the method comprising:
- forming a pattern of at least one metal precursor material on a surface region of a substrate; and
 - causing conversion of the metal precursor material to a metallic material under RTP conditions.
- 66.** The method according to claim 65, wherein the metallic material is formed on a different substrate.
- 67.** A pattern or object obtainable by the method according to any one of claims 1 to 60.
- 68.** The pattern or object according to claim 67 being electrically conductive or transparent.
- 69.** The conductive pattern or object according to claim 67, being substantially free of metal oxide at the time of manufacture.
- 70.** The pattern or object according to any one of claims 67 to 69, for use in producing an element on an electronic device or optoelectronic device.
- 71.** The pattern or object according to claim 70, wherein the element is associated with an electric circuit or conductive interconnections.
- 72.** An element comprising a pattern or object according to any one of claims 67 to 71.

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73. A device comprising a pattern or object according to any one of claims 67 to 71 or an element according to claim 72.

74. The device according to claim 73 being an electronic device or optoelectronic device.

75. A kit comprising at least one solid surface having on at least a region thereof a pattern of a metal precursor material, the material being suitable for forming a mirror image of said pattern on a different substrate, and instructions of use.

76. The kit according to claim 75, wherein the instructions related to use of the solid surface are in accordance with RTP conditions.