

# Ink-jet fabrication of electronic components

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## Abstract

Nanosized metallic particles dispersed in a polymeric matrix have been used conventionally as a paste or ink to print electrically active patterns on different substrates. The potential of ink-jet printing in this field is clearly important but the challenge to date has been how to achieve prints of low volume resistivity from the very low viscosity ink required for ink-jet printing. In this study, ink-jet printing techniques were used to directly deposit metallic conductive patterns to produce wiring boards, antennas, electrodes and so forth. In these methods, aqueous solutions of metal salt and reducing agent were ink-jet printed consecutively onto the substrate, where an immediate chemical reduction transformed the metal cations into very fine metallic particles. The best performing reducing agent for ink-jet metal deposition was found to be ascorbic acid at neutral pH. Using this chemistry, nanosized silver patterns, composed of particles in the size range 10–200 nm, were successfully formed using a standard office ink-jet thermal-head printer. Deposited layers of silver with high electrical conductance up to  $1.89 \times 10^5 \text{ S m}^{-1}$  and sheet resistance up to  $0.5 \Omega/\square$  were printed whilst higher conductivities might be expected using more appropriate devices.

(Some figures in this article are in colour only in the electronic version)

## Introduction

Direct printing of metals from aqueous solution is an important target for the ink-jet printing of electronic components; a liquid-based ink which would finally deposit a solid metallic pattern in a digitally defined procedure on different substrates is highly desirable. A major challenge in applying ink-jet processes for direct writing and metallization is the formulation of suitable inks. The inks must contain the appropriate metal precursors and a carrier vehicle. In addition, they may contain various binders, dispersants and adhesion promoters, depending on the nature of the precursor and the particular application. In the case of inks for metallization, the content of the metal precursor ink must be adjusted to provide

the required resolution with good adhesion and the desired electronic properties for the final conducting printed patterns. Ink composition is critical because it defines the way in which the ink can be jetted, the adhesion to the substrate, the line resolution and profile, and controls the mechanism of metal formation [1].

There are several approaches to formulate the metal precursor inks. They can be composed of dissolved organometallic compounds or polymers, colloidal suspensions of metal nanoparticles or some combination of these constituents. Using organometallic inks, the desired material is formed upon thermal decomposition of the organometallic molecule which contains the atom or atoms of interest in the final materials. Using metallic nanoparticles in an organic or

polymeric vehicle or adding them to the organometallic ink is another option for enhancing the electrical behavior of the final prints [2, 3].

It is important to have an ink formulation which is compatible with the particular ink-jet system chosen for deposition. When the colloidal inks are used, the particles should be small with no agglomeration tendency in order to prevent clogging of the jet nozzles, in addition to having properties such as viscosity and surface tension within the range specified for the ink jet. Generally, piezoelectric-driven ink-jet heads are more suitable for deposition techniques than thermal ink jets, where the drop is produced via formation of a bubble by locally overheating the precursor. Overheating can cause premature decomposition of the precursor inside the printer head and nozzles, thus compromising the performance of the jet [4].

For direct metal printing using an ink-jet device, some applications propose the use of an ink-jet printer to apply a promoter type material such as tin chloride ( $\text{SnCl}_2$ ) or catalytic palladium to a substrate prior to exposing the substrate to an electroless deposition process. In this procedure, the final deposition of metals from the metallic salt solution takes place over the ink-jet pre-printed catalytic patterns. The problem is that this approach requires the use of electroless deposition solutions and chemical stabilizers which can be aggressive in nature and environmentally toxic [4].

A more interesting alternative is to deposit metal directly onto the substrate using a fluid applicator such as an ink-jet printer. In direct deposition at least two fluids, which react to give the desired material for a range of applications, emerge from separate printing heads. Thus, multiple printing steps are used to deposit different reagent solutions that react together to form solid products. The main advantage of this technique is that reagents may be prepared in a solvated form and formulated into printable inks, which are able to pass easily through any printing mechanism. Solid product can be formed either during the process of print transfer to the substrate or on the printed surface itself. Moreover, this technology allows manufacturers to deposit different materials advantageously from multiple ink-jet heads to prepare a wide range of reaction scenarios in the form of user-defined patterns which may be sequences of differing layers [5–12].

In 1996 Agfa-Gevaert [13] first patented a process for producing a lithographic printing plate by ink-jet printing an aqueous solution of a silver salt and a reducing agent on an anodized aluminum substrate. The patent was based on information-wise projection droplets of a reducible silver compound, a reducing agent and physical development nuclei that catalyze the reduction of the silver compound to silver metal after placement on the substrate. Silver acetate, lactate, salicylate, etc were used as soluble silver compounds, and the preferred nucleation materials were colloidal metallic particles which catalyzed the reduction of the silver salt to silver metal. The reducing agent(s) applied in this process could be any kind of developing agents used in silver halide photography, such as the polyhydroxy-benzene type of reducing agents. The lengthy and multi-stage process, using very toxic chemicals in the developing and fixing process, makes the invention unsuitable for the rapid and environmentally friendly procedures demanded nowadays in most production sectors.

A patent application published in 1997 [14] disclosed a method for producing a metal-coated non-conductive substrate by contacting a substrate with a solution of a noble metal compound in such a manner that the noble metal ions are adsorbed at the substrate surface. In the second step, the substrate was treated with a non-contaminating reducing agent to reduce the surface-adsorbed noble metal ions to their elemental state. In the final stage, coating of the substrate with a metal in an electroless metal-plating bath takes place to form a metal-coated substrate. Using this method, the substrate to be metallized is immersed in an electroless plating bath; however the method is not suitable for direct selective metallization.

Another patent revealed a method to form silver coatings on ceramic filters. In this application, the surface was first sensitized by applying a solution comprising the silver–ammonia complex salt produced by mixing silver nitrate and ammonia until a brown precipitate is formed. This brown precipitate ( $\text{Ag}_2\text{O}$ ) re-dissolves in excess ammonium hydroxide giving a solution known as Tollen's reagent. It is well known that this solution when sprayed on a surface that has been pre-sprayed with an aldehyde solution forms a thin silver coating. This method is especially suitable for the silver coating of ceramic filter materials but is not applicable for selective metallization or metallization of substrates with limited adhesion properties [15].

In a series of patents, a similar plating method has been deployed but in this case a catalyst-containing primer coating was formed by application of a primer material. Subsequently, the metal salt solution and a reducing agent are sprayed from separate spray nozzles leaving a well-adhered layer of conductive metal on the substrate. The chemically formed metallic layer is capable of electroplating to build up the metal layer; the primer is responsible for bonding the layer to the substrate [16, 17].

QinetiQ in 2003 [5] patented the concept of depositing solid materials directly onto a substrate by using a fluid applicator such as an ink-jet printer. According to this invention's concepts, a printed circuit board (PCB) could be printed by an ink-jet printer by simply printing the metal salt and the reducing agent directly instead of two colors from a conventional ink-jet printer. Based on this theory, one of the printing fluids proposed was a compound of cobalt, nickel, gold, silver, palladium or copper, while the other component, which reduces the metal compound to free metal, can be a reducing agent such as one or more of a hydrophosphite, a hydrazine, a borane or amino-borane, glucose, borohydride, aldehydes, tartrates and tin(II) compounds.

The procedure patented by QinetiQ almost covers the whole concept of using ink jet in material deposition although it does not describe a simple, safe reducing chemical that would find ready use in practice. Some of the suggested reducing agents in the patent description such as glucose and aldehydes are unable to reduce the metallic compounds to the metal under the ambient conditions usually used in a conventional ink-jet printing process. On the other hand, the toxicity of some of the reducing systems and their polluting risks raise serious questions.

Although there is growing potential use for ink-jet processes in the electronic industry, no report has seemed to

suggest an easy, user-friendly, environmentally safe and cheap process for ink-jet metal deposition on different substrates, using commercially available ink-jet printers. Thus, our specific goals are to show the feasibility of using ink-jet technology to deliver an aqueous metal salt solution and then a safe, water-soluble, non-odorous reducing agent to print highly conductive patterns with low contact resistance and good resolution on various flexible substrates.

## Materials and methods

### Chemicals

Sodium and zinc formaldehyde sulfoxylate were obtained from BASF along with Cyclanon ECO, all as commercial grade materials. Chemicals such as ascorbic acid (83.3%), hydroxylamine, sodium borohydride, copper salts, i.e. copper sulfate, copper nitrate, etc. and silver salts, i.e. silver nitrate, carbonate, acetate, chloride, etc. were purchased from different chemical suppliers (Avocado, Lancaster, Fluka and Aldrich). Copper sulfate and silver nitrate, as the main metallic salts used in the experiments, were laboratory grade and all other chemicals were selected as analytical grade.

Different substrates were used in the final ink-jet metal deposition tests including A4 size copying paper, A4 size ink-jet transparency film and woven fabrics made up of 100% cotton. A4 size copying paper of  $80 \text{ g m}^{-2}$  (80 GSM) and transparency films (polyester film with hydrophilic coating) were purchased from Guilbert. 100% bleached cotton fabric (plain weaved,  $190 \text{ g m}^{-2}$ ) was obtained locally (from Whalley, Bradford).

### Ink-jet deposition plan

For printing purposes a Hewlett Packard (HP) single head office ink-jet printer (Apollo 1200) was used to print metallic salt and/or reducing agent solutions in separate runs. Usually the substrate was first printed with the reducing ink and then with metal precursor ink. Microsoft Word was used as the printer controlling software. The substrate could be an A4 size sheet of paper, an ink-jet transparency film or a piece of fabric glued to paper.

A full deposition cycle in a two-ink (metal salt and reducing agent) printing format is pictorially shown in figure 1.

In this cycle, after opening and washing the ink-jet printer cartridges, they were loaded separately with aqueous reducing agent and metal salt solutions. In each printing sequence, the cartridge was placed into the printer and the first pattern was printed on the substrate. Intermediate drying prevented subsequent contamination of the printer rollers in contact with the printing surface; the second cartridge loaded with metal salt was then used to ink jet exactly on top of the previously (reducing ink) printed areas. Metal formation occurred *in situ* as a consequence of the redox reaction between reducing agent and metal salt solutions leaving metallic layers composed of aggregated metal particles. The thickness of the deposited layer may be increased by repeating the ink-jet deposition process.

Non-reacted residues of reducing agent and metal salt can act as impurities between the deposited metallic particles

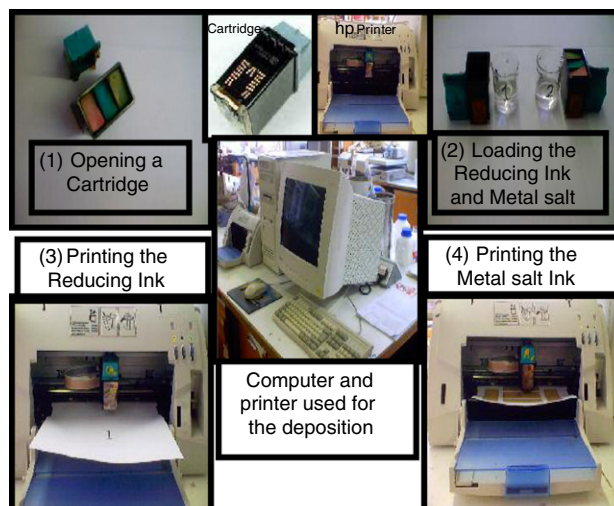


Figure 1. A full ink-jet deposition cycle starting from cartridge preparation.

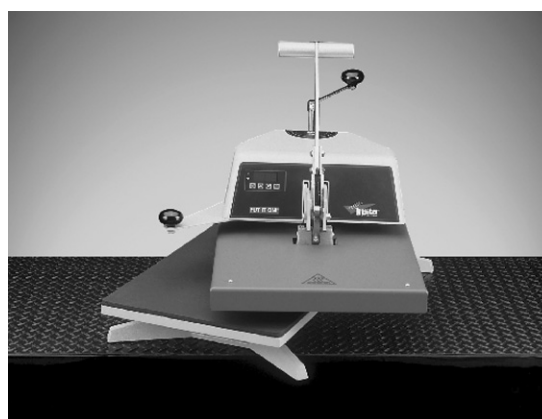


Figure 2. Hot press equipment for the dry extraction process.

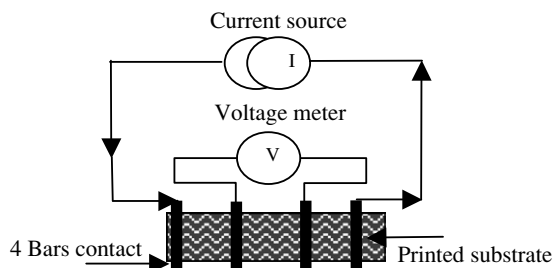
and should be extracted in an after-treatment process. Gentle washing with water is a very simple method of extracting highly water-soluble impurities. Hot extraction was another method used in which a clean paper sheet was pressed on top of the dried deposited surface at high temperature (i.e.  $> 100 \text{ }^\circ\text{C}$ ) using a transfer printing press (figure 2).

### Conductivity measurements

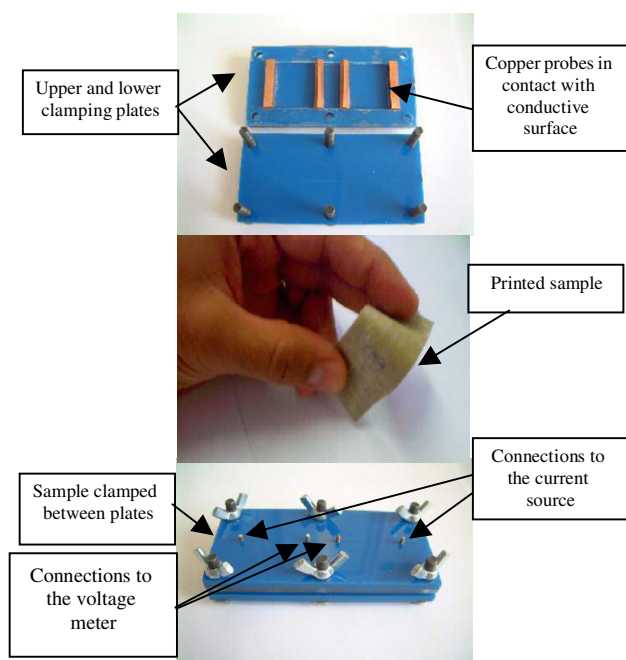
The final metal deposited patterns were tested for conductivity using the appropriate equipment. The conductivity of the films provides a measure of the underlying microstructure since any discontinuities or anomalies arising from the deposition process would lower conductivity. The electrical conductivity ( $\sigma$ ) is a measure of how well a substance passes electrical current and may be determined from the resistivity ( $\rho$ ) which is the inverse of conductivity. Resistivity may be determined through the following relationship:

$$\rho = \frac{Vtw}{Il} \Omega\text{m}$$

where  $V$  is the measured voltage,  $t$  is the sample thickness in meters,  $w$  is the sample width in meters,  $l$  is the sample length in meters and  $I$  is the inputted current in amperes.



**Figure 3.** Circuit diagram of a four-contact measuring apparatus.

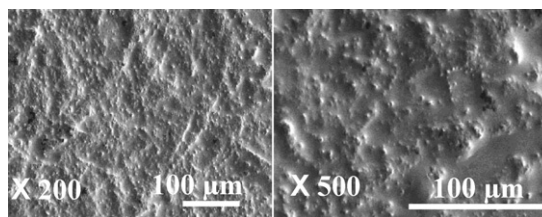


**Figure 4.** Schematic presentation of the four-contact measuring device.

A four-contact method was used in preference to the four-point probe method usually employed in the electrical assessment of films [18]. A circuit diagram of the four-contact apparatus which is designed and built is shown in figure 3. For each measurement, the ink-jet metal deposited sample was clamped in between two plates; one of these plates was fabricated with four copper probes which could contact the sample surface (figure 4).

Metal-deposited samples with a minimum length of 80 mm and of different print widths were measured; the actual length used in the resistance calculations was 10 mm, which was the distance between the two inner probes (figure 6). To obtain accurate readings, the sample was secured between two plates using six screws which gave consistent and proper contact between their surface and the copper probes.

After clamping the sample between the plates, a constant current of 100 mA was supplied to the outer probes and the voltage between the inner probes was measured using a voltmeter. In this way, an average value of resistivity over the width of the film strip (i.e. effectively the integration of an infinite number of four-point probe measurements across the strip width) could be obtained. To minimize measurement errors mainly caused by inconsistent contact



**Figure 5.** SEM images of an ink-jet copper deposited pattern on paper.

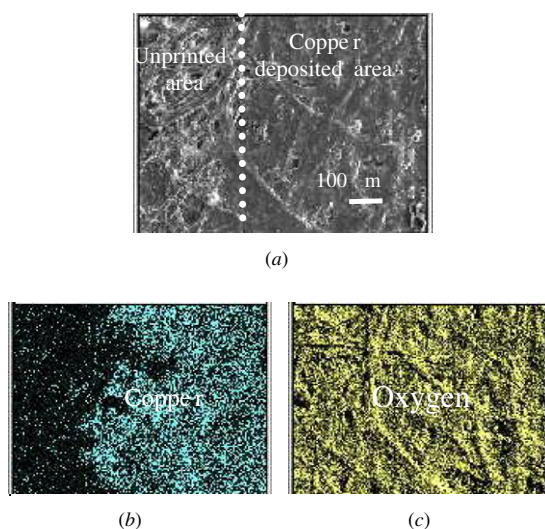
between the copper probes and the printed surfaces, each sample was tested three times and the average value was used in calculations. The thickness of the deposited metallic layers was measured under a scanning electron microscope (SEM) using the position tagged spectrometry (PTS) attachment to map metallic elements present in the deposited cross-section.

## Results and discussions

### Copper ink-jet deposition

To formulate a suitable ink-jet ink capable of depositing copper on the printed substrate, it is vital to find the best reducing agent and copper salt. Sulfur-containing reducing agents such as sodium dithionite, sodium thiosulfate, zinc formaldehyde sulfoxylate (Decrolin), sodium formaldehyde sulfoxylate (Rongalit C) and Cyclanon ECO along with sodium borohydride, thiourea dioxide and ascorbic acid were evaluated. Three reducing agents, Decrolin, Rongalit and ascorbic acid, had the ability to precipitate conductive copper particles in solution experiments, and were selected for ink-jet deposition trials. Ascorbic acid was found to be the only reducing agent able to transform copper ions into solid particles after ejection of both solutions onto the substrate. Using ascorbic acid, ink-jet deposited aqueous solutions of copper sulfate (20%, w/v) could be reduced to a brown, stable, non-conductive deposit. Replacing copper sulfate with copper nitrate in this ink-jet deposition trial did not show any sign of copper deposition as the compound obtained returned to its original blue non-reduced form after a short time.

In a series of experiments, aqueous solutions of copper sulfate (20%, w/v) at pH 2.5 and ascorbic acid (49%, w/v) at different pH values (between 2 and 8) were loaded into separate color ink-jet cartridges and printed sequentially on A4 paper using the HP Apollo ink-jet drop-on-demand printer. Loading two solutions into separate containers of a color cartridge was not possible as they could react at the surface of the nozzle's plate, immediately after ejection, causing a clogging problem related to metallic copper formation over and inside the nozzles. Using two separate cartridges for metal salt and reducing inks provides the possibility of printing one of the inks in the first step and over-printing it with the other ink in the next step. The ascorbic acid solution was printed on ordinary copying paper in the first step, dried at room temperature for 5 min, and then in the second step the pattern was over-printed with copper sulfate solution (20%, w/v). In this way an ink-jet copper deposited pattern was produced by repeating the above ink-jet printing cycle five times. The metallic printed sample was observed under the scanning electron microscope (SEM), and the SEM images are shown in figure 5.



**Figure 6.** Elemental mappings of a washed ink-jet copper deposited paper ( $\times 200$ ). (a) The SEM image of a copper deposited paper after washing with water. (b) Position tagged image of (a) for copper. (c) Position tagged image of (a) for oxygen.

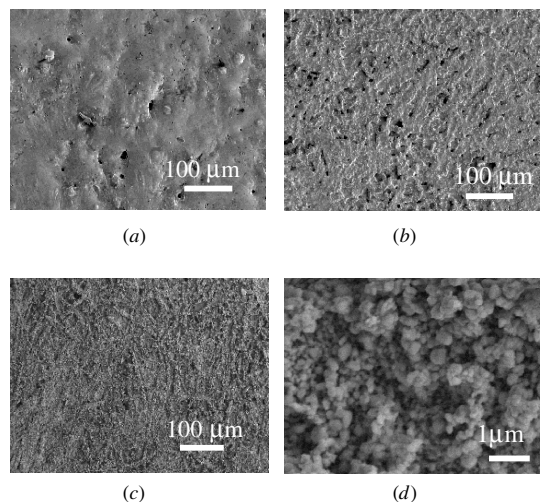
As seen in the SEM images, the deposited layer contains clusters of solid particles distributed in a homogenous phase. SEM position tagged spectroscopy was used over the copper deposited area and the adjacent unprinted parts of the paper to check the formation of copper oxide during the ink-jet deposition process. The ink-jet deposited samples were cut from the edges of the deposited patterns to include the unprinted parts of paper for an easy comparison of the paper and the deposited layer's contents. One of the copper deposited patterns was washed using distilled water for 5 min to remove most of the soluble impurities including the excess reducing agent and copper salt residues, and then dried at  $80\text{ }^{\circ}\text{C}$  for 15 min. The elemental mapping procedure for elemental oxygen and copper was carried out on washed and unwashed samples. The actual SEM micrograph and the elemental mapped images of the washed samples are shown in figure 6.

The presence of excess oxygen of copper oxide during the ink-jet deposition process was a problem since it rapidly converted some of the metallic copper formed in the printed areas to copper oxide.

Because of the presence of oxygen in the printing atmosphere and as none of the deposition trials could ultimately deposit electrical conductive copper, attention was switched to the deposition of another metal. Subsequently, silver was selected since its standard reduction potential is nearly three times that of copper and it is of reasonable price; it also has a long history of application in the electronics industry.

#### Silver ink-jet deposition

Silver has been used for centuries to reduce bacteria growth as well as being a key component in electronics. From a toxicological point of view and unlike other metals such as lead and mercury, silver is not toxic to humans and not known to cause cancer, reproductive or neurological damage, or other



**Figure 7.** SEM images of a five-layer ink-jet silver deposited pattern on paper. (a) Five layers of silver deposited on paper (unheated and unwashed) ( $\times 100$ ). (b) Five layers deposited and pressed to a clean paper at  $150\text{ }^{\circ}\text{C}$  for 20 s ( $\times 100$ ). (c) Hot pressed ( $150\text{ }^{\circ}\text{C}$ , 20 s) and washed with water spray ( $\times 100$ ). (d) Hot pressed ( $150\text{ }^{\circ}\text{C}$ , 20 s) and washed with water spray ( $\times 8000$ ).

chronic adverse effects. Nor has normal day-to-day contact with solid silver coins, spoons or bowls been found to affect human health. This is because solid silver is almost completely biologically inert, and even if ingested, would pass through the human body without being absorbed into tissues. Silver nitrate is attractive as a potential metallic silver-bearing ink because of its high water solubility, stability and reasonable price.

Ink-jet deposition of silver from silver nitrate solutions was most effective when using either ascorbic acid or hydroxylamine as reducing agent. Although hydroxylamine gave conductive prints, because of its irritant and possibly toxic nature, further ink-jet deposition experiments used ascorbic acid as the reducing substance.

A 40% (w/v) solution of ascorbic acid (pH 7–7.2) and a 67% (w/v) silver nitrate solution (pH 6.5) were used in the ink-jet silver deposition trials. The reducing ink was printed first and after an intermediate partial drying at room temperature for 5 min the silver nitrate was overprinted. To extract the unreacted chemicals and their residues after the redox reaction, the silver deposited pattern was washed with water for 30 s and then hot pressed against a clean sheet of paper at  $150\text{ }^{\circ}\text{C}$  for 20 s (hot extraction). Some yellow residual compounds, extracted from the printed pattern, are transferred to the clean paper during this hot pressing process. The magnified SEM images of the prints after the washing and hot extraction processes are shown in figure 7.

As is clearly visible (in the highly magnified image), the ink-jet deposition process is capable of producing nanosize silver particles on the substrate. A high concentration of the silver-bearing ink and fast reduction of silver ions to metallic silver are the main reasons for the formation of the particulate structure. Particle growth in a vertical direction has caused the formation of a very rough surface containing clusters of nanosize particles. The horizontal growth of each particle is usually limited by the growth of adjacent particles leading to a high degree of contact between the nanoparticles.

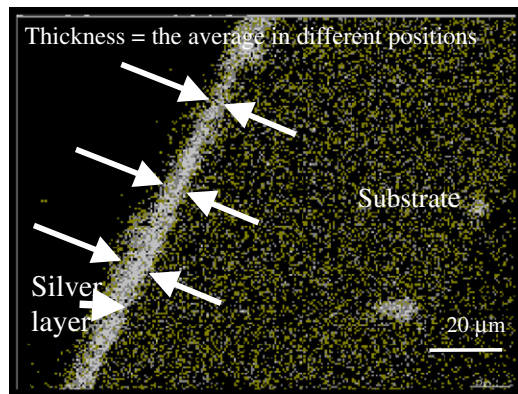
**Table 1.** Maximum conductivity of the ink-jet silver patterns deposited on different substrates.

Substrate	Deposition sequence	Measured resistance ( $\Omega$ )	Thickness ( $\mu\text{m}$ )	Pattern width (mm)	Pattern length (mm)	Resistivity ( $\times 10^{-5} \Omega \text{ m}$ )	Conductivity ( $\times 10^5 \text{ S m}^{-1}$ )
Paper	AG	3.57	3	9.5	10	1.02	0.983
	AGAG	0.354	5	29	10	0.51	1.948
	AAGG	1.208	4	9	10	0.43	2.299
Ink-jet transparency film	AAG	3.96	3	9	10	1.07	0.935
	AAGAG	0.42	4	29	10	0.49	2.053
Cotton fabric	AAAGAG	3	5	29.5	10	4.43	0.226
	AAAGAGAG	0.871	6	26	10	1.36	0.736

**Table 2.** Comparison between the averages of the best conductivity achieved on ink-jet deposited samples and bulk metals.

Ink-jet deposition on (substrate)	Highest conductivity ( $\times 10^5 \text{ S m}^{-1}$ )	Sheet resistance ( $\Omega/\square$ )	Cond. <sup>a</sup> to silver	Cond. <sup>a</sup> to copper	Cond. <sup>a</sup> to graphite	Cond. <sup>a</sup> to steel
Paper	1.890	0.588	0.0030	0.0033	2.7000	0.0172
Transparency	1.53	0.934	0.0024	0.0027	2.1857	0.0139
Cotton fabric	0.693	2.405	0.0011	0.0012	0.9900	0.0063

<sup>a</sup> Cond. = conductivity compared.

**Figure 8.** Cross-sectional silver position tagged SEM image of an ink-jet deposited pattern (on a transparency film) indicating an area of silver layer thickness measurement ( $\times 500$ ).

The spherical shape of the deposited nanoparticles can be a consequence of them being surrounded by reducing agent and silver salt residues which could prevent full contact in a multi-surface network.

Ink-jet silver deposited in rectangular shaped patterns was prepared on three kinds of substrates (paper, transparency film and cotton fabric) and cut out for conductivity measurements. Each pattern was prepared using a different deposition sequence where each ink was ejected over the previously printed layer after an intermediate drying step. The conductivity was then measured. To measure the thickness of each deposited layer, the distribution map of elemental silver in the cross-sectional SEM image was used (figure 8).

Final calculated conductivity values are shown in table 1 for ink-jet deposited patterns on paper, ink-jet transparency film and cotton fabric. The minimum resistance values shown in the table are the result of dividing the measured voltage between the inner probes by the current applied to the outer probes of the four-contact device. The letters A and G in the deposition sequence column stand for ink-jet printing of ascorbic acid (A) and silver nitrate (G) inks, respectively.

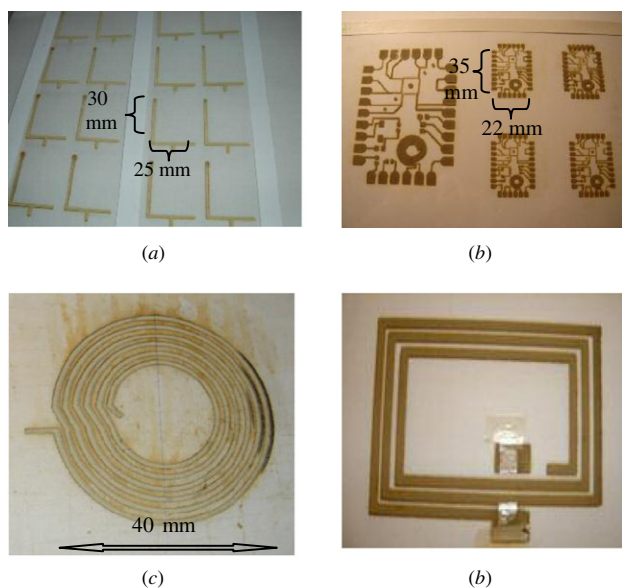
Table 1 illustrates the capability of the ink-jet deposition technique to produce layers with conductivities lower but comparable to that of bulk metals and much better than graphite.

In table 2, the maximum conductivity obtained on each substrate is compared with the conductivity of bulk metals and graphite. The average value of all readings according to the best deposition sequence for each substrate was used as the highest conductivity. Sheet resistance was calculated after dividing the resistivity of each deposited layer by its thickness. The conductivity values of bulk metals were then divided by the best conductivities calculated for the deposited layers (table 2) in order to assess the conductivity ratio of the deposited layers compared to bulk metals.

A simple comparison between the sheet resistance values of the ink-jet deposited layers and the resistance of available inks and paints ( $\approx 0.03\text{--}0.5 \Omega/\square$ ) readily reveals the capability of the ink-jet deposition technique to deposit highly conductive patterns on different substrates. Using a suitable printer with higher resolution and better controlling software, and pre-treating the surfaces to give a more regular texture, should ultimately improve the print conductivities to a range closer to that of the commercially available conductive inks containing silver and copper nanoparticles. All the deposited patterns, even with the present setup, showed a higher conductivity compared to patterns produced with graphite and carbon containing pastes.

Printing PCBs, which are conductive tracks, can be simplified using the present deposition process as it is capable of depositing conductive tracks along with resistors and capacitors. A low conductivity track will work normally as a resistor and two parallel conductive lines can form a capacitor. The ink-jet technology described can deposit conductive tracks in the form of antennas for different devices such as mobile phones or radio frequency identification (RFID) tags. Some of the deposited silver patterns produced in the present research are shown in figure 9.

Ink-jet deposition of silver was also used as an alternative to the screen-printing method for efficiently depositing silver

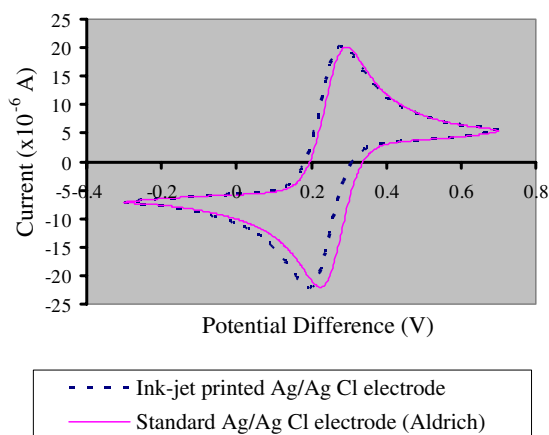


**Figure 9.** Some of the deposited silver patterns for different applications. (a) Mobile phone antennas on the transparency film. (b) Wiring boards printed on the transparency film. (c) Inductive coil printed on fabric. (d) RFID antenna with metallic joints printed on paper.

to build a silver/silver chloride reference electrode for electrochemical and biosensor purposes. Potassium chloride can be easily dissolved in the ascorbic acid solution or can be used in a separate cartridge which after mixing with silver nitrate could deposit a mixture of silver and silver chloride. The product contents depended on the ratio of reactants present in the reaction; ink-jet ejection can provide a very selective method of dosing different amounts of each chemical in different positions.

To test the capability of the ink-jet deposition method for printing reference electrodes, solutions of ascorbic acid (20%, w/v, pH 7.2), silver nitrate (20%, w/v, pH 6.5) and potassium chloride (3.5%, w/v) were loaded separately into the ink-jet cartridges. Simple patterns were ink-jet deposited using the AAGGGG sequence on paper. Patterns then were ink-jet printed with repeated ejections of potassium chloride and heat treated at 130 °C for 30 s. Washing was carried out on the deposited patterns to remove all soluble materials, which will include excess potassium chloride, excess reducing agent and silver nitrate residues. After drying, two layers of potassium chloride were ejected over the patterns for completion of the electrode structure.

Printed patterns were then glued to a polyester film for better handling during the electrochemical tests using a mixture of fluorocarbon and acrylate resins in equal portions. Deposited electrodes were then cut and coated with a fluorocarbon resin (water proofing agent) with one end kept out of the resin to allow enough contact between the testing solution and the printed surface. The performance of the ink-jet printed reference Ag/AgCl electrode was compared to a commercially available silver/silver chloride electrode (from Aldrich) in cyclic voltametry of ferrocyanide ( $\text{Fe}(\text{CN})_6^{3-}/\text{Fe}(\text{CN})_6^{4-}$ ). The experiment was carried out once using a commercial electrode and the next time with



**Figure 10.** The performance of an ink-jet printed Ag/AgCl versus a commercially available reference electrode in cyclic voltametry of ferrocyanide.

the ink-jet printed reference electrode. The ink-jet printed electrode's performance versus the commercial Ag/AgCl electrode performance is shown in figure 10.

The similarity of the graphs in figure 10 points out that the performance of the ink-jet printed electrodes is very acceptable, making this method of producing sensors a very good alternative to the reference electrodes currently used in bio-sensor testing and production procedures.

Silver is not usually recommended for use as the working electrode in electrochemical analysis because of its reactivity, especially with halide ions. Although it could not be used in all electrochemical applications, the printed silver patterns were tested for a possible application in sensing procedures. A series of electrochemical analysis revealed the great potential of the deposited silver for usage in sensing electrochemical processes. The silver electrode was inert to the species present in the electrochemical testing solution, in a specific range of potential difference, whilst showing a reproducible response with acceptable stability and robustness.

## Conclusions

The key point in designing a user and environmentally friendly ink-jet chemical deposition process is to find the best reducing system capable of reducing metal salts in ambient conditions with the lowest risk to the environment and operators. Ascorbic acid was found to be an excellent safe reducing agent, giving a successful deposition of metallic patterns on different substrates.

Copper sulfate was found to be a promising salt because of its good water solubility and ease of reduction. The main difficulty in all copper ink-jet deposition experiments was that copper oxidation occurred during the deposition process. To ensure that copper metal production was the main outcome, it would be necessary to control copper oxide formation and this would add technical complexity to the process; it is likely that a nitrogen atmosphere would be required.

Silver was thus selected for deposition in order to develop an environmentally/user friendly and practical method for chemical deposition of conductive patterns; silver is the second most widely metal used in the electronic industry.

Silver nitrate was selected as the silver precursor in the ink-jet deposition process because of its very high water solubility, reasonable price and availability. Silver nitrate and ascorbic acid could deposit silver metal on water absorbing surfaces whilst the surface structure and its interaction with the inks can affect the conductivity level of the deposited layer.

According to the SEM observations, ink-jet deposited particles are attached to each other, limiting the level of enhancement in their compactness upon application of external pressure. Clearing the surface of non-metallic deposits in the deposited pattern and completion of the reduction reaction by a hot extraction process led to improvement of electrical conductivity.

The movement of ink droplets on the substrate after ejection can change the achievable resolution and the feature size (the smallest size of a complete component deposited on a substrate such as paper). For instance, on a normal copying paper with no particular pre-treatment, the minimum width of a silver deposited feature was around 100  $\mu\text{m}$  using a printer with 300 dpi resolution and Microsoft Word processing software. These limitations are mostly imposed by the printing hardware, and using a more appropriate ink-jet printer with higher resolution can automatically provide the possibility of printing smaller features (around 10  $\mu\text{m}$ ).

Ink-jet silver deposition on hydrophobic substrates, such as uncoated polyester film, using water-based inks was found to be very difficult. Although the deposition inks could react to deposit silver particles on such a water repellent surface, the lack of droplet spreading and efficient film formation prior to particle deposition was the main obstacle toward formation of a continuous conductive layer.

The level of conductivity achieved by the ink-jet deposition approach was found to be highly dependent on the surface properties of the substrate. Ink-jet deposition on paper can produce higher conductivity because of its smoothness compared to fabrics and the coated layer of ink-jet transparency film. Ink-jet deposited silver patterns on paper were found to be almost 300 times less conductive than silver wires and 3 times more conductive than solid graphite. The sheet resistance of ink-jet deposited patterns was also comparable with conductive pastes available in the market. Although ink-jet deposited patterns could not achieve conductivities as high as bulk metals, their level of conductivity can be sufficient for some specific electronic applications.

Ink-jet deposition processes can be employed for printing PCBs, antenna devices, electrodes and generally in any application where their level of conductivity and surface properties are acceptable. Compared to commercially screen or off-set printed antenna devices on polymeric substrates, the ink-jet deposited antenna on paper showed similar electrical conductivity.

Ink-jet fabrication of the silver/silver chloride (Ag/AgCl) reference electrode was used as another application for the ink-jet deposition process in the construction of electro-chemical measuring devices. The ink-jet printed reference electrode performed very accurately in electrochemical experiments, matching the performance of a commercially available silver/silver chloride electrode.

Ascorbic acid was found to be the most valuable reducing agent for the ink-jet deposition process and its use may be

a breakthrough in direct write ink-jet printing technology for building electronic components. Although printing a high quality pattern, appropriate for use in the electronics industry, needs more research, the present findings in conjunction with the advanced capabilities of recently available ink-jet printers mark a starting point for a safer, low cost and digitally controllable method for the build-up of metallic patterns on hydrophilic flexible substrates.

Low consumption of materials, very limited wastage in energy and chemicals, digital control over the ejection and positioning process, user friendliness, etc are some of the advantages realized on replacing conventional production techniques with ink-jet procedures.

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