Continuous ink-jet printing electronic components using novel conductive inks

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Abstract

To reduce the cost of electronics fabrication and to take advantage of numerous potential specialized applications, a novel process of manufacturing three-dimensional electronic products is introduced in the present investigation. This process, which is currently being patented by the University of Pittsburgh, utilizes specialized continuous ink jet (CIJ) printing technology and innovative conductive inks that are capable of producing high-resolution conductive traces. Unlike drop-on-demand (DOD) techniques that are aimed at more precise features sizes (1 micron or less) and smaller scale applications, the present investigation demonstrates that the new process can be used in mass production applications where larger feature sizes (~50 microns) are sufficient. It has been found that the traces produced by the process have excellent adherence and have an electrical resistivity of only 2.9 times of bulk silver after curing. The major advantage of the proposed CIJ process is that it not only provides a fast and cost-effective method for applying electronic components (conductors, diodes, capacitors and resistors) on existing products, but it also allows the printing of conductive traces in three-dimensional space. With a throw distance that exceeds 10 cm, it demonstrates how the new fabrication process is not only suitable for desktop microfabrication, but also for large volume applications such as automotive glass.

Introduction

Advances in photolithography techniques have allowed the electronics industry to miniaturize components over the past several decades. Based on these advances, new technological challenges have emerged because of the limited geometric flexibility, increased processing complexity, increased processing time and greater cost of existing fabrication methods. In today's global marketplace, therefore, there is a strong need to introduce innovative fabrication techniques that can produce high quality products using processes that are both faster and cheaper than traditional methods. In this light, inkjet printing technology offers several potential advantages over direct write fabrication processes including low capital equipment costs, high materials efficiency, rapid deposition rates, and increased flexibility in the creation of geometric features. In the electronics industry, for example, inkjet printing of circuit interconnects is an additive process where material is only deposited on specified locations, thereby minimizing the amount of material utilized in the circuit board formation process. In fact, in a fully integrated inkjet system, an entire circuit trace patterns could be designed using computer graphics software and printed directly onto a substrate. This is in contrast to conventional screen-printing techniques that require sophisticated masks. Inkjet printing techniques, therefore, offer a higher degree of automation that will help minimize cost and increase repeatability and reliability.

There are two different ink-jet techniques that have become mature in the printing industry: drop-on-demand (DOD) and continuous ink jet (CIJ). In a DOD system, single drops are ejected through an orifice at a specific point of time. To maintain accuracy, a DOD printing head must be placed vertically above and very close to a substrate (within 1mm). Continuous inkjet systems, in contrast, utilize a pressurized fluid stream and a piezoelectric element to form droplets. By oscillating the piezoelectric element at high frequencies (in the range of 20 to 80 kHz), capillary waves are generated within the fluid domain to break up the fluid stream (fig.1). By carefully adjusting the voltage and frequency of the PZT device, a continuous and consistent stream of fluid droplets of uniform size and spacing can be generated. By placing conductive material in the fluid, an electric charge can be impressed on selected drops as they break-off from the fluid stream at the center of a charge channel as shown in the figure 1. These charged droplets can then be deflected by means of high voltage deflector plates to form various patterns onto the substrate. The uncharged droplets are captured by a gutter mechanism and re-circulated through the system.

The flexibility, precision, and speed of the CIJ printing process has allowed it to be used in numerous applications within the coding, marking, and labeling markets, as well as the textiles and micro-manufacturing industries [1,2]. CIJ offers benefits over DOD with respect to image quality, throw distance, and the ability to deflect droplets independent of gravity [3,4]. These advantages make CIJ capable of printing components in three-dimensions (figure 2), which has been the focus of our research at the University of Pittsburgh for the past several years [5].
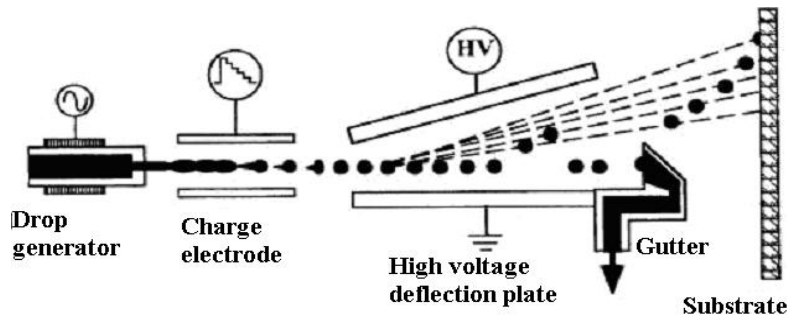

Figure 1 Continuous ink-jet printing: A multiple-deflection system [10]

Figure 2 Three-dimensional pigmented CIJ printing in coding and marking (resource: www.linx.co.uk)
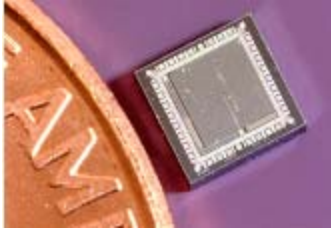
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Figure 3 PENI tag

Inkjet printing is most commonly utilized in desktop office printers, but there are numerous other applications that can incorporate ink-jet printing technology. Electronics and biomaterials are the two fields to offer significant potential for utilization of the inkjet printing process. Precision micro dispensing based upon ink jet technology has been used in biomedical applications since the early nineties. It is a key enabling technology in the development of Bio-MEMS devices, bio-molecular sensors, micro-fluidic devices and micro-optical systems [6]. The printing of sensors on medical components, for example, can be tailored to meet specific requirements. The market for manufacturing biomedical sensors has been estimated to exceed several billion dollars [7]. Low-cost RFID tags that are expected to replace UPC barcodes on consumer products, likewise, can be printed using CIJ technology to achieve enhanced consumer convenience and warehousing efficiency through a realization of real-time controls, automated inventory processes and automated checkout [8]. Recent research by the investigators on small antennas has made it possible to fabricate the antenna directly onto the chip as a part of the CMOS fabrication process (fig.3). Such a change in the design removes the cost of assembling a separate antenna. Microsystem devices such as resonant inductive coils, electrostatic-drive motors, and actuators can be constructed with ink-jet printing methods [9].

Current Conductive Inks

A major challenge in utilizing inkjet processes for printing electronic components is the formulation of inks with suitable physicochemical properties. Specifically, the rheology properties of the conductive inks must be compatible with available inkjet printing technology. The surface tension and viscosity of the ink determines the ejected droplet velocity, size, stability and the shape of the droplets impinging on the substrate [10]. The impingement shape establishes trace resolution and thickness, which ultimately determine the trace mechanical and electronic properties. Inks possessing a surface tension on the order of 25-70 mN/m and Newtonian viscosity of 1-10 mPa have shown to be most suitable for use with the CIJ processes (Table 1 [11]). Most commercially available conductive inks possess viscosity and surface tension that exceed levels which allow droplet formation in the range of 30-100 μm size using ink jet technology [12].

To satisfy the requirements of inkjet printing, the inks must contain the appropriate precursors and carrier components. Various binders, dispersants, and adhesion promoters are generally included in the composition, depending on the nature of the precursor and the particular application. In the case of inks for metallization, the content of the metallic ink must be adjusted to provide the required resolution, adhesive and electronic properties for the conducting lines. Conductive inks are based on noble metals because of their chemical inertness

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and electrical conductivity [13]. There are several categories for ingredients of conductive inks including nanoparticles, microparticles, and metal organic decompositions.

Table 1 Typical ink properties for a continuous ink-printer [11]

Viscosity (cps)	1-10
Surface tension (dynes/cm)	25-70
Particle size	Micrometer, no agglomerate

1. Nanoparticles

Nanoparticles typically measure 1 to 100 nm in diameter and consist of clusters of metallic, semiconducting, or insulating atoms. Because of their small size, nanoparticles exhibit melting temperatures as low as $1000^{o}C$ below their bulk material [14]. The lower melting point is a result of their comparatively high surface-area-to-volume ratio, which allows soldering bonds to take place between neighboring particles at relatively low temperatures. Nanoparticles can be sintered at plastic-compatible temperatures as low as $300^{o}C$ to form a material that is nearly indistinguishable from the bulk material. Their low melting temperature is a major reason that gold and silver nanoparticles can be used as a precursor for conductive ink. Unlike micro scale particles, nano-size particles will not clog a typical 30 μm inkjet orifice, making them capable of producing high-resolution components. The Media Laboratory at MIT has made conductive inks by dispersing 5-7 nm diameter silver particles that are 10% by weight in alpha-terpineol into a colloid. The printed silver was found to have a resistivity of approximately 3uΩ.cm, which is approximately the twice that of the bulk silver (1.6uΩ.cm) [9]. Researchers at University of California Berkeley have reported a conductive ink of thiol-encapsulated 1.5 nm gold nanoparticles that were dissolved in toluene or alpha-terpineol [15,16].

2. Metal Organic Decomposition (MOD)

Metallo-organic crystals can be dissolved in an evaporable organic solvent such as toluene, ethanol or butanol to form conductive inks. Metal films can form upon solvent evaporation and decomposition of the metallo-organic compound during curing. In the process, gaseous byproducts of the decomposition leave the system, providing contamination-free metal films. Computer controlled ink jet assisted metallization of the grid pattern of solar cells with metallo-organic decomposition (MOD) silver inks offers a maskless alternative method to conventional photo-lithographic thin film technology and screening technology [17]. By curing at a low temperature ($350^{o}C$) after direct printing, a uniform line film on rough surface solar cells has been found to be a low-cost, fine-resolution, and convenient process. The National Renewable Energy Laboratory reported the inkjet printing of metal organic decomposition (MOD) inks that had good adhesion and measured a contact resistance of 400 $\mu\Omega.cm^{2}$ [18,19].

3. Micro-scale metal particles

US patent **6,036,889** disclosed the formulation of a conductive ink formed of a mixture of metal flakes and metallo-organic decomposition (MOD) compounds in an organic liquid vehicle [20]. The mixture contains metal flake with a ratio of the maximum dimension to the minimum dimension of between 5 and 50. The MOD compound begins to decompose at a temperature of

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approximately about 300°C to promote consolidation of the metal constituents and bonding to the substrate in a time less than six minutes. The addition of silver flake to the MOD compound allows thicker deposition without loss of resolution. By adding silver colloidal with a mean particle diameter of approximately 20 nanometers, the temperature for consolidating the metal has been further reduced to 270°C [20]. Heating the deposited material to temperatures just above about 300°C results in consolidation of the material to near theoretical density with electrical resistivity of around twice that of the bulk metal and good mechanical properties. The current limitation of the micro-scale metal particles is that it is too thick to be inkjet printed with standard techniques.

4. Aqueous solution of silver inorganic compound

Nano scale particles or MOD precursors are two general resources for synthesizing conductive inks whose rheology properties permit inkjet printing. They work well under small-scale experimental conditions, but resources are expensive and sometimes not available commercially. In the current research, the investigators have developed a novel aqueous ink composition for CIJ printing that can be broadly applied. The precursors are commercially available and substantially less expensive than metallo-organic compounds. Due to its low cost, silver nitrate was chosen as the primary inorganic compound in an aqueous ink composition. Silver nitrate is used in almost all processes for producing silver compounds and has a wide range of applications that vary from painting, xerography, chemical electroplating, electric batteries and medical catalysts. Silver nitrate melts at 212°C and decomposes to silver at temperatures from 440°C to 500°C. It also has solubility of 219 g in 100gram water, which is significant when very dense ink is needed for high-resolution electric circuits. Considering the broad resources and physical properties, silver nitrate makes an excellent candidate if it satisfies other basic prerequisites for conductive inks. Silver chloride is another important silver compound, but it has a high melting temperature of up to 455 °C and is only slightly soluble in water, making it unsuitable for the conductive inkjet printing.

Applied Inkjet printing system

The investigators have constructed a specialized continuous ink-jet system for depositing conductive ink materials. Originally designed and developed at the Swanson Center for Product Innovation (*www.engr.pitt.edu/SITE/SCPI*), this modular system can produce conductive traces on glass and polymers. Overall, the system consists of three major components: (1) a specialized print head, (2) a control system, and (3) a dual-axis precision positioning table.

As shown in Figure 4, the constructed print head includes all of the standard mechanical components required for continuous ink-jet printing – a PZT can, a sapphire orifice, a charge tunnel, deflector plates, and a gutter. In the print head (top view), the charge tunnel is 6 mm in diameter, the deflector plates have dimensions of 30 mm by 10 mm, and the sapphire orifice was 60 μm in diameter. In addition to these mechanical components, the figure shows the underside (bottom view) of the print head, which contains a PCB board and all of the electronic circuitry required to control and generate the droplets. In the print head, the PZT can was 0.8 inches in diameter and included a 0.2 in-diameter PZT element. The fluid stream being deposited by the print head is controlled using the control system depicted in Figure 5a. The control system

contains a reservoir for the material being deposited and allows direct variation of numerous system variables. These variables include the fluid system pressure, the material flow rate, the voltage applied to the PZT crystal (controls deflection), the vibrating frequency of the PZT crystal, and the electrical properties of the charge tunnel and deflection plates. The final component of the current experimental CIJ system is a dual-axis, precision motion table. The positioning table, which is depicted in the experimental set-up shown in Figure 5b, is computer programmable and has an accuracy of 100 nanometers.
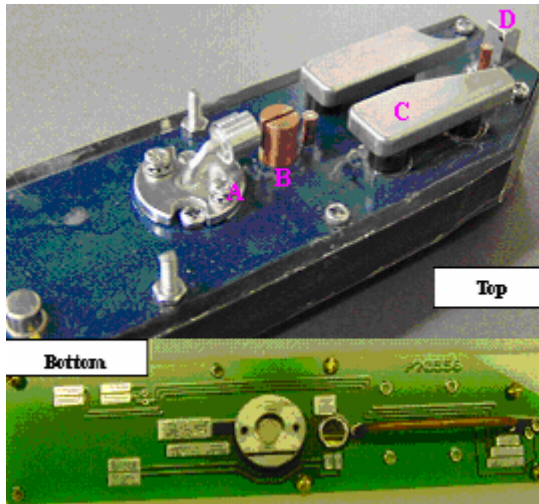

Figure 4. CIJ printing head: A - Orifice; B – Charge tunnel; C – Deflection tunnel; D – Gutter
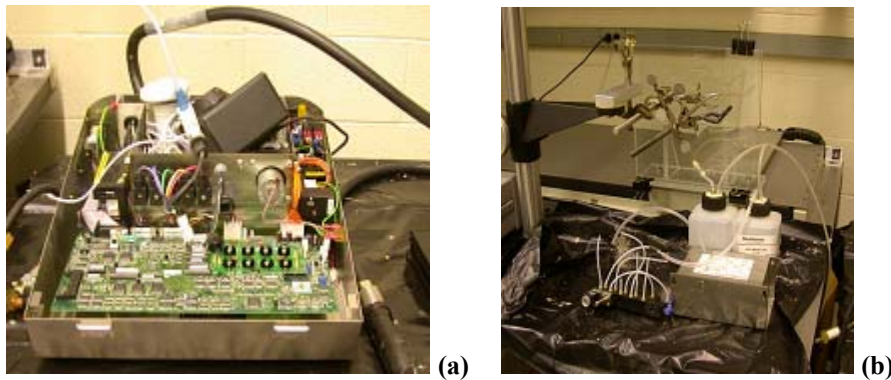

Figure 5. (a) CIJ printing control system; (b) Motion table.

Experimental procedure and results of novel aqueous conductive ink

Primary experiments were carried out by printing an aqueous solution of 0.5 gram silver nitrate diluted in 1 ml pure water. After being printed on a glass substrate and cured at 500°C for 15 minutes, the structure shown in Fig 6 was obtained. As demonstrated by the figure, the trace was neither aesthetically appealing nor functional. After analysis, the white thick film in the figure was found to be metallic silver and the black net-shape material was determined to be the metal oxide. The decomposition was observed to be so violent that small drops were exploded and dispersed nearby. When heated above 212°C, the surface tension of the liquid silver nitrate increased significantly and the slim trace broke and contracted to separate spots on the glass substrate. The final cured trace was therefore discontinuous and had no real application as an

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electric conductor. The adherence of the solid spot to the glass substrate could be easily peeled off, further showing the inability of a simple silver nitrate solution to form a smooth continuous conductive trace. Additives were deemed necessary to change the characteristics for the applications of interest. Specifically, the additives were needed to modify the aqueous silver nitrate to address the following requirements:

    a. To slow down the decomposition process of the silver nitrate and make it controllable;
    b. To adjust the surface tension of the melted silver nitrate at high temperatures;
    c. To bond metal silver thick films with glass substrate inherently;
    d. To be chemically and physically compatible with a silver nitrate water solution.

To improve the properties of the silver nitrate solution, numerous chemical additives were selected, tested, and compared based on their physical and thermodynamics properties in the solution together with the silver nitrate. Some additives were found to be effective in improving the conductive silver nitrate ink. In this manner, a viable conductive ink was produced by combining 25~100 gram of silver nitrate, 10~25 gram of additive chemicals and 100 ml of pure water into a transparent aqueous solution. The material was then printed using the CIJ system onto micro glass slides heated to 75°C. The heated glass substrate was found to increase the evaporation rate of the ink, thereby decreasing the width of the trace produced. It is important to note that substrate temperatures above 100°C were avoided because a porous trace structure developed from boiling. The printed solution was dried and crystallized on the glass slide. The glass slides were then put into a stove that was preheated to 485°C. After 20 minutes curing, the silver nitrate solution homogeneously decomposed into a shining metal trace. The color of golden yellow was observed from the opposite side of glass, which indicated intimate chemical bonding of the printed traces onto the glass substrate.

Figure 7 shows a SEM structure of the conductive trace that was produced after curing. In the figure, there are many 'cell-like' substructures composed of silver conductive film. The silver has a purity of 95% and produces good electric conductance. There are openings for the metal silver cells, which assure silver conductivity between cells. This property is crucial for continuous conductive traces in a macro-scale because the slightest amount of discontinuity will make the trace nonconductive as a whole. The durable metal oxide ridge surrounds the silver cells to protect the soft silver film from wear and also allows it to strongly adhere to the glass substrate. This special functional composite structure explains the traces' beneficial characteristics. In fact, the pure silver in the developed compounds did not naturally produce a strong adherence with glass. The interlayer of oxide, therefore, should be considered a necessary component for attaining a strong adherence to the glass substrates.

As listed in table 2, the novel ink has surface tension and viscosity properties that are similar to pure water. The surface tension can be adjusted in the range of 25~70 dynes/cm to satisfy CIJ printing demands and without affecting the final trace characteristics. Compared to the ink properties for the continuous inkjet printers listed in table 1, the new ink is fully compatible with current CIJ technology. It is noteworthy to mention that there is no clogging problem during the inkjet printing process after several days of continuous operation.
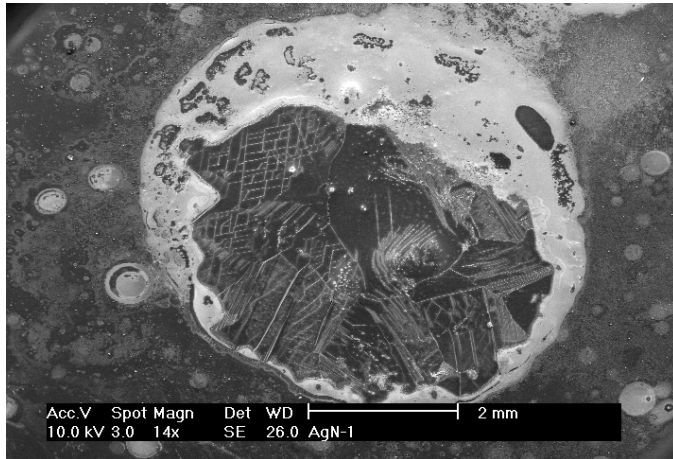
Figure 6 The SEM photo of decomposition debris after silver nitrate was thermal decomposed on glass slide.

Table 2 Fluid properties of normal and dense ink applied experiments.

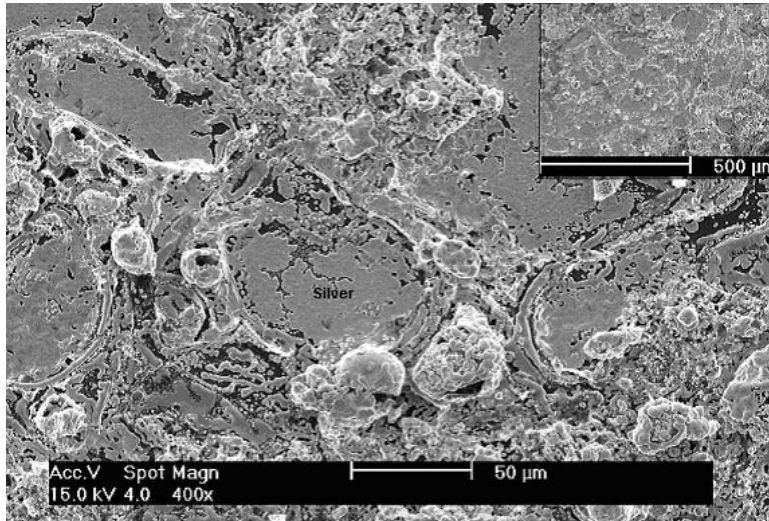|	Normal	Dense
Density (g/ml)	1.4	1.68
Viscosity (cps)	1.47	2.58
Surface tension (dynes/cm)	68	82

Figure 7 Microstructure of conductive trace after novel conductive ink was cured at 485°C for 20 minutes.

Results

Once the preliminary ink solution was obtained, a factorial design was carried out to determine the critical processing parameters for optimizing the conductive inks. Based on the factorial design, optimized ingredients of 0.2 gram of additives with 1.0 gram of silver nitrate in 1ml water were determined. These ingredients were sufficiently stirred until all the components were completely dissolved and a transparent aqueous solution was achieved. The aqueous solution was then printed with the CIJ system onto a micro slide glass substrate. The glass substrates were heated on a hot plate to 75°C and then cured at 485°C for 20 minutes.

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The electric resistance of the optimized ink was measured to be between 0.4~0.6 ohm per inch. As measured by a Surtronic 3+ profilometer, for a typical single-pass printed conductive trace, the trace thickness was measured to be 1.8μm and the width was 1.3mm. The resistance was 0.5 ohm per inch length and the electric resistivity was calculated only 2.9 times of bulk silver ($4.6E^{-8}ohm*meter$). The sheet resistance was 0.0256 ohm/square in this case. The silver conductive trace was firmly bonded to the glass substrate. Abrasion tests were carried out using a pin-on-disk tribometer with the parameters set as:

Abrasion tool: ½ inch (Diameter) steel ball
Tip loading: 125g, 250g, 500g
Running circle radius: 15 mm
RPM: 75

After the pin-on-disk wear experiment, no abrasion of the trace was observed after 1000 cycles under a load of 125g when viewed under a microscope (Fig 8). In-time monitoring of electric resistance along both sides of cutting point during abrasion tests further confirmed the strong adherence of conductive trace to glass substrate (Fig 9.) For a 125 gram tip loading, abrasion was observed to start only after 2500 cycles and the trace was broken after 5000 cycles. The conductive trace withstood up to 1600 cycles when the loading was kept as high as 500g. The results from the abrasion test demonstrated that the current ink can be safely applied in the situations where frequent scratching takes place on the surface of conductors, for example, windshield heaters. In fact, the abrasion results far exceed current industry standards.
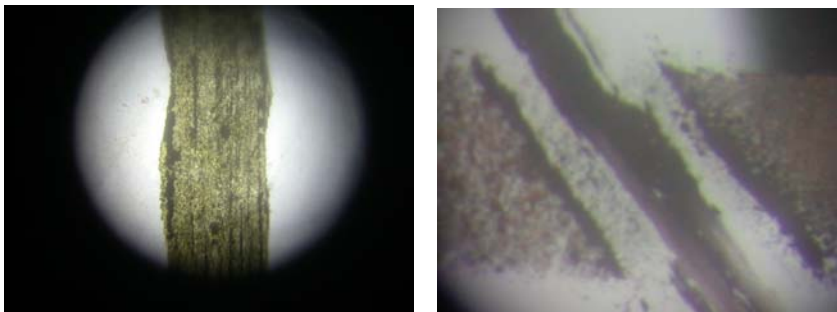

Figure 8 Abrasion was not observed on the conductor printed with current ink after 1000 runs (Left);
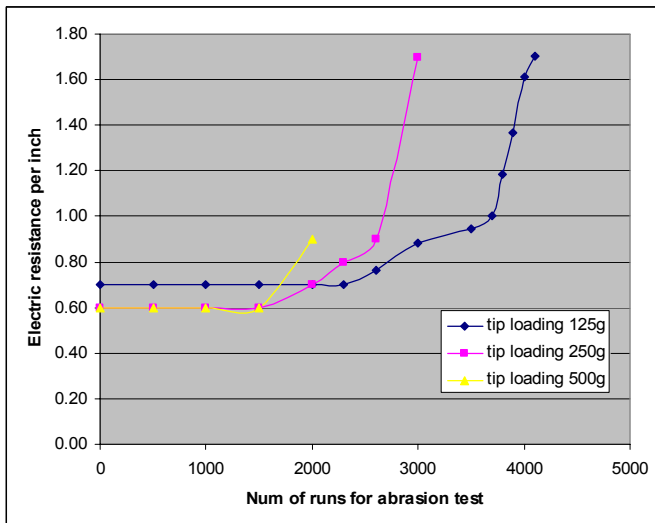**Abrasion of the conductor with the ink printed using glass frit as adherence promoter after 300 runs (Right).**

Figure 9 Electric resistance change during 5000 runs of abrasion test, tip load: 125 g, 250g and 500g, respectively.

Applications

Once the aqueous conductive ink was generated, the continuous ink jet system developed by the investigators was used to produce conductive traces on glass substrates. The investigators found that uniform size and constant ink droplets could be generated and controlled without satellites disturbance (figure 10) by adjusting the fluid pressure, the voltage and frequency of the PZT crystal, and the charge tunnel pulse. Droplet diameters produced were in the range of 100μm and the droplet velocity was approximately 4m/s. This material was found to possess good viscosity and surface tension properties and was able to produce conductive traces (Figure 11) similar to windshield heating grids after heating at 485°C for 20 minutes. The resolution of the grid lines were approximately 0.4 mm and the printed sample produced 0.5 watts per square inch at approximately 3.5 volts, which was well within the required range for a windshield.

As a preliminary experiment to determine the three dimensional capabilities of the CIJ system, a spiral conductive trace was produced on the outer surface of a small glass cylinder (Figure 12). The glass bottle was preheated for fast material evaporation so that undesirable trace flow was reduced. The final trace produced had uniform thickness, good electric conductance (resistance of $4.6E^{-8} ohm*meter$) and a strong adherence to the glass substrate. To further demonstrate the ability to print in three-dimensions, antenna patterns were printed on the inner surface of a bugle-shaped glass cup. To print the patterns, the cup was fixed on the 2-D motion table at a 45° angle to the axis of the inkjet head, as indicated by the dashed lines in figure 13(a). With precision modulation of the droplets and control of motion table, the printed traces on the three-dimensional curved surfaces were continuous and of consistent quality (figure 13b). Two very important characteristics of the printed system are demonstrated in traces shown in Figure 13b. First, the system is capable of producing quality traces over a very long throw distance, as the length from the orifice to the bottom of the bugle shaped cup is about 4 inches. Secondly, the angle between the axis of orifice and the normal axis of deposited surface varies from -45° to 45°, which demonstrates that the CIJ technique is capable of printing on complex 3-D surfaces.

Summary:

In an effort to reduce the cost of electronics fabrication, novel conductive ink materials are introduced in the present investigation that are capable of being printed in three-dimensions, using CIJ technology. Based on experiments performed using an inkjet printing system developed by the investigators, the following conclusions can be drawn:

1. Specified aqueous silver ink solution can be inkjet printed to produce conductive metal patterns that have sufficient electric properties for use in commercial applications.
2. The most important ingredient in the aqueous ink is silver compound, i.e. silver nitrate. Commercially available additives are required to make the silver nitrate a better conductive precursor. And the aqueous ink can be prepared instantly by simply mixing the ingredients with water. This makes the aqueous ink inexpensive, convenient, and compatible to the current CIJ technology.

3. Based on wear tests using a pin-on-disk tribometer, the ink produces conductive lines with impressive adherence to glass substrates. In addition, the traces produced had an electrical resistivity of only 2.9 times of bulk silver after curing.
4. Utilizing a cylindrical glass cylinder, the investigators showed that the new process was able to print the conductive traces in three-dimensional space. It is believed that further refining the CIJ process and ink material will allow the process to be used in the electronics fabrication industry.
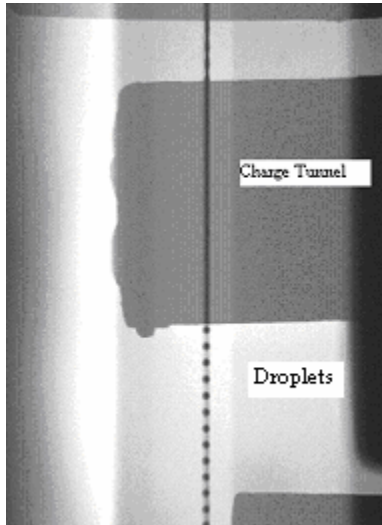

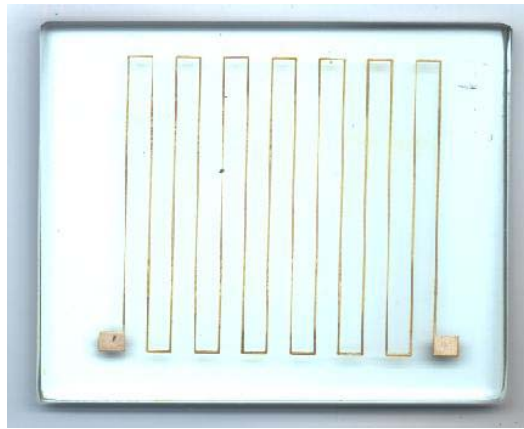**Figure 10 Stable droplets generated and charged from CIJ system**

Figure 11 Sample silver heating grid
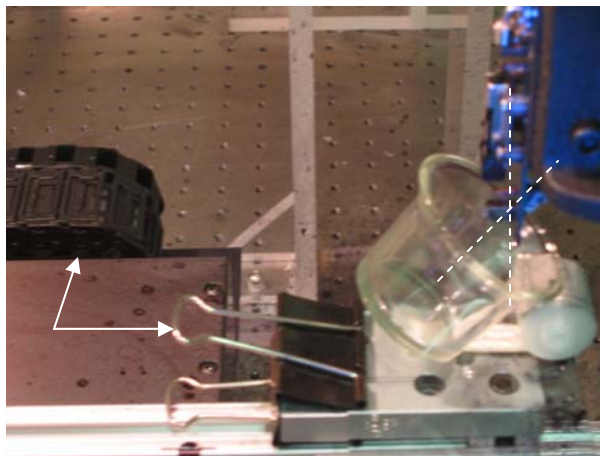
Figure 12: Spiral Conductive Trace

Figure 13 (a) The cup was fixed on the 2-D motion table; (b) Antenna pattern was printed on the 3-D inner surface of bugle cup with CIJ printing.

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