FORMULATION AND PROCESSING OF CONDUCTIVE INKS FOR INKJET PRINTING OF ELECTRICAL COMPONENTS

by

Junfeng Mei

B.S. in Material Science and Engineering, Hefei Technology University, 1994

M.S. in Mechanical Engineering, Tsinghua University, 1997

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SCHOOL OF ENGINEERING

This dissertation was presented

by

Junfeng Mei

It was defended on

Sept, 15, 2004

and accepted by

Dr. Marlin Mickle, Professor, Electrical Engineering Department

Dr. Laura Schaefer, Assistant Professor, Mechanical Engineering Department

Dr. Frederick Pettit, Professor, Materials Science and Engineering Department

Dr. Roy Marangoni, Associate Professor, Mechanical Engineering Department

Dissertation Director: Dr. Michael Lovell, Associate Dean for Research and
Associate Professor, Industrial & Mechanical Engineering Department

ABSTRACT

FORMULATION AND PROCESSING OF CONDUCTIVE INKS FOR INKJET PRINTING OF ELECTRICAL COMPONENTS

Junfeng Mei, PhD

University of Pittsburgh, 2004

A novel process utilizing specialized continuous inkjet (CIJ) printing technology and innovative conductive inks to fabricate three-dimensional electronic products is introduced in the current investigation. The major advantage of the CIJ process is that it not only provides a fast and cost-effective method for applying electronic components, but it also allows the printing of conductive traces in three-dimensional space. The greatest challenge for inkjet printing of electrical circuits is the formulation of the conductive inks, which define not only the convenience of the materials being deposited, but also the final comprehensive properties and the major expense. Several conductive inks were investigated and compared mainly based on their electric conductance and mechanical adherence to a substrate.

Two different particle-free solution conductive inks were specifically researched for low cost, deposition convenience and improved properties. A novel aqueous solution of silver nitrate with a corresponding adhesion promoter is introduced for the first time. It has been found that the traces produced by the process have excellent adherence and have an electrical resistivity of only 2.9 times that of bulk silver. Low temperature curing plus further annealing of a specified metallo-organic decomposition (MOD) ink produces close-packed silver crystal substructures. The electrical conductance of the final conductive trace was close to that of bulk silver, and wearability was significantly improved from ductile deformation. These two particle-free solution inks are expected to find a number of applications in various industries.

Fundamental concepts in formulating and post-processing of inkjet printing are fully discussed. The two primary problems faced by inkjet printed components are low deposited thickness and porosity. An interlayer oxide film was found to be necessary to bond the precious metal layer with the glass substrate. Porosity can be significantly reduced through high temperature annealing, which not only increases electrical conductance, but also mechanical strength. Special curing methods are proposed to consolidate the printed conductors and avoid overheating of temperature sensitive substrates.

DESCRIPTORS

3-Dimensional
Aqueous Solution Ink
Conductive Ink
Consolidation
Continuous Inkjet Printing
Direct-Writing
Electrical Circuits
Metallo-Organic Decomposition
Nano Particles

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1.0 INTRODUCTION

Current methods of fabricating electric circuits make use of selective masking and etching technologies to create regions of conductive metals on nonconductive substrates [1]. Such practice not only waste expensive metal materials, but also generates substantial amounts of chemical pollutants. In addition, this method does not lend itself to automation because of the required lengthy substrate processing steps. In today's global marketplace, however, 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.

To meet these challenges, a novel process of manufacturing three-dimensional electronic products is introduced in this dissertation. This process, which is currently being patented by the University of Pittsburgh, utilizes specialized continuous inkjet (CIJ) printing technology and novel deposition materials to produce conductive traces and electronic components on a wide range of substrates, including the product case or structure. The major advantage of the proposed process is that it not only provides a fast and cost-effective method for applying conductive lines on existing products, but it also allows the printing of conductive traces in three-dimensional space. The proposed technique has already garnered significant interest in several industrial sectors. This commitment is based on the belief that the research is both on the cutting-edge of innovation and directly applicable for the next generation of new products. Despite showing significant promise, the current process has required fundamental research to be performed before it could be utilized in a production environment. Specifically, in order to be directly incorporated into an on-line manufacturing process, substantial research has been conducted to determine the optimum of each of the following:

(1) Formulation of the conductive inks being deposited, which is the major focus of this dissertation;

(2) Design of the mechanical and electrical components in the specialized continuous inkjet system.

It is believed that this new process will have a significant and broad impact by eliminating the need for costly masks that are limited to a two-dimensional space. If it is realized to construct 3-D circuits directly on products, there are far reaching applications through many industrial fields and great improvements in design and fabrication of current commercial products and processes.

1.1 TRADITIONAL FABRICATION METHODS FOR ELECTRICAL CIRCUITS

1.1.1 Photolithography

Photolithography is the process of transferring geometric shapes from a pattern mask to the surface of circuit boards. There are seven steps involved in the photolithographic process: wafer cleaning, barrier layer formation, photoresist application, soft-baking, mask alignment, exposure & development and hard-baking. In the first step, the wafers are chemically cleaned to remove any trace impurities on the surface. After cleaning, silicon dioxide is deposited on the surface of the wafer, serving as a barrier layer. After the formation of the silicon dioxide layer, high-speed centrifugal whirling, known as "spin coating," produces a thin uniform layer of photoresist on the wafer surface. Almost all of the solvents are removed from the photoresist coating by the soft-baking process, which plays a very critical role in photo-imaging. Only after soft-baking do the photoresist coatings become photosensitive, or imaginable. One of the most important steps in the photolithography process is mask alignment. A mask is a square glass plate with a patterned emulsion of metal film on one side. The mask is aligned with the wafer, so that the pattern can be transferred onto the wafer surface. Once the mask has been accurately aligned with the pattern on the wafer's surface, the photoresist is exposed with a high intensity ultraviolet light through the pattern on the mask and the solubility pattern of the resist is then developed. Exposure to the UV light changes the chemical structure of the resist so that the photoresist becomes soluble in the developer. The exposed photoresist is then washed away by the developer solution, leaving windows of the bare underlying material. Hard-baking is the final step in the photolithographic process. This step is necessary in order to harden the photoresist and improve adhesion of the photoresist to the wafer surface.

The main advantage in photolithography lies in its capability for building high resolution feature up to sub-100nm. For general electrical applications where a 50-200 micron resolution is acceptable, photolithography is an excessively complex method of seven-step. Since the mask prototyping and fabrication are time-consuming and expensive, the patterning on each wafer is essentially a deductive process, during which the precious materials are wasted, some of the wasted materials are detrimental to the environment, and most importantly, the long lead time makes photolithography sluggish in response to flexible market changes. Considering the expensive mask for prototyping, photolithography generally is only suitable for large bulk scale manufacturing to reduce the cost of a unit product.

1.1.2 Screen printing

The use of silk or other closely woven fabrics or meshes to carry patterns has a long history. The patterns leave some of the mesh open and the rest impervious. A high viscous paste with fine particles is wiped over the screen; some of the paste is forced through a stencil pattern onto the surface of the substrate. The process is used in the production of decorative finishes, labeling of bottles and containers, and in the production of etched or printed circuit boards. One of the primary advantages of screen printing is the ability to transfer a pattern of materials onto a substrate at a high rate. Areas of 40 by 60 cm^2 can be transferred in times on the order of 1 minute, and line widths of around 100 microns can be attained. After drying or firing, the thickness of the materials deposited by screen printing is on the order of 10 microns [2].

Similar to photolithography, screen printing is a manufacturing method with masks. It results in wasted materials, a long lead time to market, difficulty for automation, etc. To improve upon the shortcomings of conventional photolithography and screen printing, a maskless alternative method for grid patterning with computer-controlled inkjet printing conductive inks is discussed in the following subsection.

1.2 INKJET PRINTING

In recent years, there has been a growing research interest in the technology of printed electronics in various applications. Inkjet printing, as a derivative of direct-write processing, offers the additional advantages of low cost, a very high materials efficiency, elimination of masks, and non-contact processing, during which droplets of ink are ejected from a small aperture directly to a specified position on a substrate to create electronic patterns. In a fully integrated inkjet system, inkjet printing permits circuits to be deposited directly from CAD files and eliminates the need for special tooling or masking. Each circuit can be different, if desired, for coding and prototyping. This is in contrast to conventional screen-printing techniques that require sophisticated masks, and for which engineering changes on the printed circuit board assembly are prohibited once the mask prototyping has been completed. Inkjet printing techniques, therefore, offer a higher degree of automation that will help minimize cost and increase repeatability and reliability. Inkjet printing is less limited by substrate composition and morphology, and can accommodate a greater number of layers and range of materials. The state of the art inkjet heads will allow minimum feature sizes lower than 20 microns, which is enough for various industry applications [3].

The inkjet printing of conductive materials has several practical applications. Electronics and biomaterials are the two fields to offer the greatest opportunities and challenges for inkjet printing processes. The underlying idea for the current research project actually originated from the manufacturing limitations of integrated circuits that are used in the field of Radio Frequency Identification (RFID). RFID is a wireless substitute for barcodes and employs readers that do not require a specific orientation for scanning, thus achieving enhanced consumer convenience and warehousing efficiency through a realization of real-time controls, automated inventory processes and automated checkout [4]. The prohibitive factor in the full-scale implementation of this technology has been the targeted cost of 1 cent per device (chip). Such a price goal has been unachievable using standard manufacturing techniques. An RFID tag classically consists of two parts, a Complementary Metal Oxide Semiconductor (CMOS) chip and an external antenna. In the current technology the antenna is printed or fabricated onto a substrate material that acts as a self-stick label. Attaining the targeted cost is extremely difficult because of the required assembly step to attach the chip or die to the antenna.

Recent research at the University of Pittsburgh on small antennas has made it possible to fabricate the antenna directly onto the chip as a part of the CMOS fabrication process (Figure 1). Such a change in the design removes the cost of assembling a separate antenna. Hence, the complete manufacturing cost of the PENI Tag® (see Figure 1) is simply the CMOS fabrication of a chip. Knowing the size of the chip, it is possible to obtain the price of a PENI Tag directly from commercial foundries. For the first time, the cost of an RFID tag can be computed on the basis of the silicon (CMOS), and the 1-cent target can be easily attained.

The capital cost of the manufacturing facilities to handle this demand would be greater than $90 billion. An alternative manufacturing process or device concept is clearly needed to achieve full-scale implementation of RFID tags and scanners. In this light, the investigators have identified a potential solution to the manufacturing limitations in the RFID field - directly depositing conductive materials onto a multitude of substrates and products using specialized continuous inkjet print heads.

Inkjet printing methods can also be used construct microelectromechanical system (MEMS) such as resonant inductive coils, electrostatic-drive motors, and actuators [5]. Other possible applications of inkjet printing include the printing of conductive traces on glass for automobile windshield heating elements and antennas, where screen-printing is currently applied.

Precision micro dispensing based upon inkjet technology has been used in biomedical applications since the early nineties. Inkjet printing is a key enabling technology in the development of Bio-MEMS devices, bio-molecular sensors, micro-fluidic devices, and micro-optical systems [6]. Because bioactive fluids, such as proteins and DNA can be fragile and expensive, they are usually not suitable for use in photolithographic or other subtractive processes. Hence, inkjet technology can provide the means to create biosensing elements containing antibodies, antigens, nucleic acid probes, cells and cell structure, and colorimetric agents for the detection of a diverse range of biological agents, toxins and chemicals. Inkjet deposition of these materials has been of interest in the last two decades. In one application, patterns of antibodies were printed onto membranes, typically nitrocellulose, that bound the antibody for use in diagnostic assays.

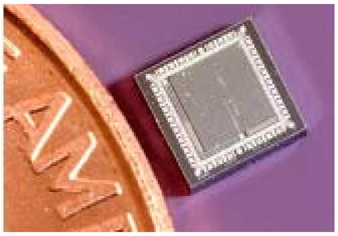

Figure 1: The PENI tag

There are two different inkjet techniques that have become mature and well understood in the printing industry for decades: drop-on-demand (DOD) and continuous inkjet (CIJ). The method of droplets being generated and controlled to move in space used by each technology is quite different, as described more fully in the following paragraphs.

1.2.1 Drop-on-demand

Drop-on-demand technology uses print head nozzles that eject a single drop of ink only when activated. Thermal inkjet and piezoelectric actuator are the two most common drop-on-demand inkjet techniques. In the drop-on-demand inkjet system, a piezocrystal expands in response to the voltage rectangular wave, causing a pressure impulse within the ink chamber, and expelling a single droplet from the orifice (see Figure 2). The chamber is refilled through the inlet by capillary action at the orifice. Thermal inkjet printers use heat to generate vapor bubbles, which eject small drops of ink through nozzles that place them precisely on a surface to form patterns or images. Originally developed for desktop printers, a thermal inkjet is designed to be inexpensive, quiet, and easy to use on flat surfaces that maintain a fixed orientation. With DOD inkjet printing, multiple small volumes of metallic, semiconducting, or insulating material can be deposited at computer-defined positions, enabling the all-additive fabrication of each device on a much faster and less expensive basis.

1.2.2 Continuous inkjet printing

CIJ is the oldest inkjet technology originally developed in the mid-1960s. Continuous inkjet systems 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 [7] (Figure 3). 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. With 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 3. 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.

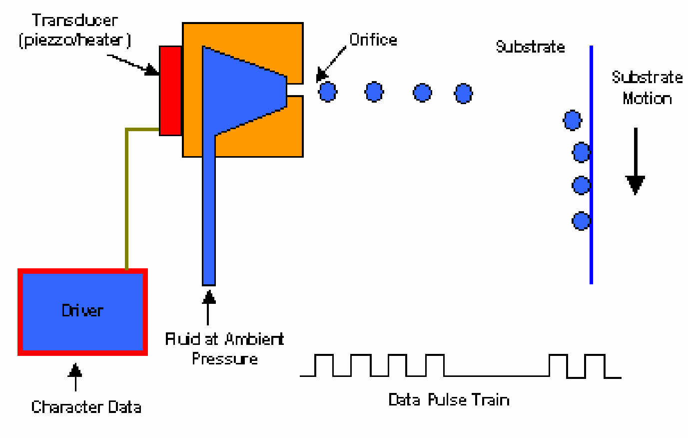

Figure 2: A piezoelectric DOD system: single droplets are ejected through an orifice at a specific point of time.

CIJ offers benefits over DOD with respect to throw distance and the ability to deflect droplets independent of gravity [8-9]. To maintain deposition accuracy, a DOD printing head must be placed vertically above and very close to a substrate (within 10 mm). In CIJ technology, the ink droplets travel a relatively long distance (at least 10 cm) before being deposited onto the substrate. The longer throw distance increases the flexibility of manipulating the substrate (larger viewing areas) and the fluid stream to produce a trace in three dimensions. The CIJ system developed at University of Pittsburgh does not depend on gravity to deposit material, which allows flexibility in the orientation of the print head. The effect of gravity can be compensated for by pressure, viscosity, and electrical charge, hence allowing printing to be performed in any direction, including vertical. Furthermore, in the CIJ technique, ejected droplets are electrically charged after exiting the orifice and later deflected to a precise location on the substrate. The ability to control and deflect the fluid particles reduces the mechanical axes in which the substrate needs to be manipulated. This reduction significantly simplifies the printing of conductive materials in three dimensions.

With a long throw distance, continuous inkjet print heads have time of flight (TOF) sensors that measure the distance between droplets. Based on TOF values, both pressure and viscosity can be tuned to optimize print quality. Having the ability to instantaneously adjust printer system parameters is greatly beneficial when printing with highly conductive materials.

The flexibility, precision, and speed of the CIJ printing process have allowed it to be used in numerous applications within the coding, marking, and labeling markets, as well as the textiles and micro-manufacturing industries [10-11] (Figure 4). These advantages come from CIJ systems' capability to print in three-dimensions, which has been the focus of our research for the past several years.

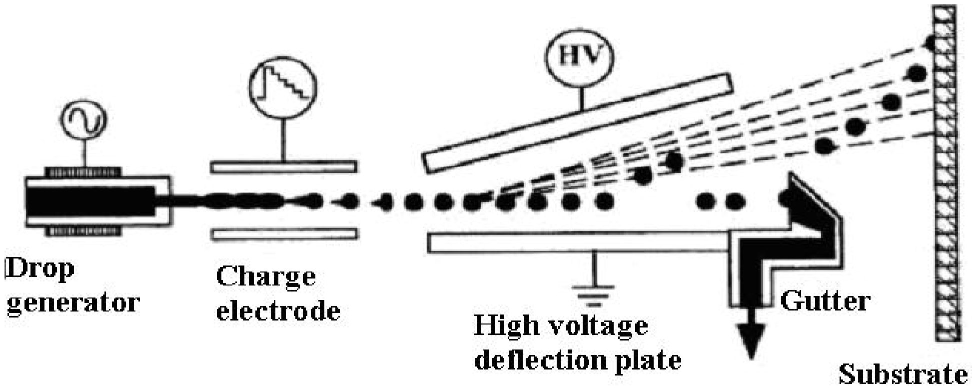

Figure 3: Continuous inkjet printing: A multiple-deflection system [7].

Figure 4: Three-dimensional pigmented CIJ printing in coding and marking (resource: www.linx.co.uk)

1.2.3 Current Inkjet Research

Drop-on-demand and continuous inkjet printing are mature technologies that have been used in consumer products for more than twenty years. Despite being well understood, researchers continue to pursue improvements in the field. At Xerox's Palo Alto Research Center, researchers have recently introduced acoustic inkjet printing (AIP) to produce photographic quality prints at speeds that compare favorably against state of the art CIJ [12]. In AIP, an ultrasonic beam is focused on the free surface of the ink to eject discreet droplets of controlled diameter. The advantage of AIP is that it is "nozzle-less" which enables generation of extremely small drops. The major limitation of AIP is that it is restricted to the printing of aqueous and wax-based inks.

Other researchers have focused on fundamental problems in the inkjet industry such as the formation of satellites and the role of substrate properties. In CIJ, smaller satellite droplets often form and follow a charged droplet, which diminishes print quality. To eliminate satellite droplets, Tseng et al. [13] have developed a thermally driven micro-injector. By extending their micro-injector design to eject solvents and fluids, they have achieved droplet volumes smaller than 1 picoliter, which is 10 times smaller than present day commercial inkjet printers [14]. Carr et al [15] studied the interaction of a single droplet with textile media to gain a better understanding of the role the substrate plays in print quality.

Recently, inkjet technology has shown great potential in several new application areas including the micro-fabrication of electronic circuitry and the development of MEMS devices. In this regard, the current research focuses on utilizing CIJ technology to fabricate three-dimensional electrical circuits as opposed to DOD, which is best suited for flat substrates and discrete device manufacturing.

1.3 OBJECTIVE OF THIS DISSERTATION

The objectives of this dissertation are as follows:

- Creating numerous conductive chemical materials that utilize a diverse set of conductive precursors, substrate binder materials, and carrier liquids for use in a continuous inkjet system to determine optimum conductive materials that can be deposited on a wide range of substrates using continuous inkjet technology;
- Performing extensive experiments to determine optimum chemical combinations and inkjet system component parameters based on the dimensional capabilities, mechanical strength, and conductivity of the traces that are produced;
- Developing the fundamental concepts and technique principles in formulating and processing conductive inks for optimum properties; and

- Demonstrating the capabilities of continuous inkjet printing to deposit materials in three-dimensional space with the specified CIJ system and conductive inks.

2.0 BACKGROUND OF CONDUCTIVE INKS

2.1 COMPOSITION OF CONDUCTIVE INKS

A major challenge in applying inkjet processes for the direct writing of electrical components is formulating inks with suitable physicochemical properties. Ink composition is critical because it defines the ejection capability of the ink, the adhesion to the substrate, and the line resolution and profile, and the mechanism of conductor formation. To satisfy the various purposes of inkjet printing, the inks must contain the appropriate 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 metal conductors, the content of the metallic ink must be adjusted to provide the required resolution with good adhesion and the desired electronic properties for the conducting lines.

2.2 PROPERTIES OF CONDUCTIVE INKS

In general, an inkjet composition must meet certain rigid requirements to be useful in inkjet printing operations. These relate to viscosity, solubility, compatibility of components, and wetability with the substrate. Furthermore, the ink is preferred to be quick-drying and smear resistant, should be capable of passing through the inkjet nozzle without clogging, and must permit rapid cleanup of the machine components with minimum effort [16]. A major problem with printing conductive metal lines using inkjet compositions is the adherence of the conductive metal lines to the substrate. This is especially the case when the substrate is glass and other oxide based materials.

The characterization methods for conductive inks are described herein. Some of the features are employed by the traditional printing industry, for example, surface tension, viscosity, etc., which determine if a certain ink is compatible with the current printing technology and can meet resolution, continuity and uniform quality requirements; some measurements are considered for the analysis of functional inks during fabrication of electrical circuits, such as thickness, electrical conductance, etc., which decide if the printed electrical devices, structures, and circuits can function properly.

2.2.1 Fluid properties of conductive inks

The rheological properties of the conductive inks must be compatible with available inkjet printing technology. The surface tension and viscosity of the ink determine the velocity, size, and stability of the ejected droplet and the shape of the droplets impinging on the substrate.

The impingement shape establishes trace resolution and thickness, which ultimately determine the trace mechanical and electronic properties.

2.2.1.1 Surface tension

Surface tension is the force acting on the surface of a liquid, tending to minimize the area of the surface; quantitatively, it is the force that appears to act across a line of unit length on the surface. Surface tension is also known as interfacial force or interfacial tension. The surface tension of water is 72 dyne/cm; some surfactants can reduce the surface tension value for water to a value in the range of 30-50 dyne/cm. A low surface tension liquid has the tendency to wet, or to spread across, a high surface tension surface. The phenomenon helps to determine whether or not the ink will remain where it is printed, and how wide it dries. The wetting characteristics of the functional ink strongly contribute to the electrical property variation, printed structure edge definition, and printing resolution.

One of the general measurement methods of surface tension is the Du Nouy ring method, in which a platinum ring of precisely known dimensions is suspended from a counter-balanced lever-arm. The arm is held by torsion applied to a wire to which it is clamped. Increasing the torsion raises the arm and ring. The ring carries with it a film of the liquid in which it is immersed, and the force needed to pull the ring free is measured. The detachment force is related to the surface or interfacial tension by $\gamma = \frac{BF}{4\pi R}$, where F is the force on the ring that causes it to break with the fluid measured; R the mean radius of the ring; and B the correction factor related to the geometry of the meniscus formed by the ring.

The drop weight method is simple compared to the Du Nouy ring method, and does not require specialized instruments. It has shown to have acceptable accuracy, and thus was applied by the author in the current investigation. The procedure for this method is to form drops of liquid at the end of tube, and then allow the drops to fall into a container until enough have been collected so that the weight of each droplet can be accurately determined. The surface tension is then calculated from $\gamma = \frac{mgf}{2\pi r}$, where m is the mass of each droplet, g is the gravity constant, f is the correction factor, and r is the radius of the tube.

2.2.1.2 Viscosity

Viscosity is a measure of a fluid's resistance to flow. It describes the internal friction of a moving fluid. A fluid with a large viscosity resists motion because its molecular interrelation gives a high internal friction. A fluid with a low viscosity flows easily because its molecular interrelation results in very little friction when it is in motion. An Ostwald viscometer tube from Sigma-Aldrich (Z275409) was used to measure the viscosity of the conductive inks. The Ostwald viscometer makes use of the rate of flow of a certain volume fluid through a capillary tube of a given length. Times were recorded for the flow of distilled water from the upper graduation mark to the lower mark and then used for calculation of the viscometer constant k. The viscosity of the measured fluid was determined following the same procedures for the calibration: $\eta = ktd$, where t is the flow time in seconds, and d is the density of the measured fluid.

2.2.1.3 Density

Density is defined as weight per unit volume of a certain conductive ink, which varies within the range of 0.8 ~ 2.0 gram/ml. Density is as significant as that of surface tension and viscosity on the generation and deflection control of the inkjet droplets.

2.2.1.4 Particle suspension

Most current commercial conductive pastes or inks include metal particles or flakes as the main conductive component. In our preliminary experiments, it was found that even particles as small as several microns in diameter could clog the inkjet orifice, and then the printing process would then be forced to stop for cleanup. There is a tendency to apply nano silver or gold colloids as conductive inks, which have less clogging problems and can be cured at a relatively low temperature to form continuous thin films on various substrates. In the current research, however, the formulation of a particle-free solution for conductive inks is preferred to reduce cost and elongate shelf life. In the following chapters, intense investigations and detailed discussion are carried out on the topics of particle-free conductive inks.

Inks with a surface tension on the order of 25-70 mN/m and a Newtonian viscosity of 1-10 mPa have been found to be most suitable for use with CIJ processes [17]. Most commercially available conductive inks possess viscosities and surface tensions that exceed permitted levels, and thus do not allow droplet formation in the range of 30-100 μm in size using inkjet technology [18]. Continuous and Drop-On-Demand inkjet technologies have different requirements for fluid properties as listed in Table 1 and Table 2 [17,19].

Table 1: Ink properties for a continuous inkjet printer

Viscosity (mPa.s)	1~10
Surface tension (mN/m)	25~70
Particle size	Micron meter, no agglomerate

Table 2: Ink properties for a drop on demand inkjet printer

Viscosity (mPa.s)	1~30
Surface tension (mN/m)	35~60
Particle size	Micron meter, no agglomerate

2.2.2 Miscellaneous Properties of Conductive Inks

2.2.2.1 Mileage

Mileage is a measure of the number of satisfactory prints that can be formed with a given amount of ink. Full scale printing presses can consume a large amount of ink. It is very important to understand the economics and cost of printing functional ink. The importance of mileage measurements to both the printer and the materials supplier will be critical in the commercialization of novel printed electronic devices.

2.2.2.2 Film thickness

The film thickness of a printed conductive trace is governed by the printing process, substrate, printing conditions, and ink properties. Accurate measurement of the film thickness enables a strong understanding of the printed structure, and provides more accurate electrical property predictions. SEM tests on the cross sections will provide insight into interfacial phenomenon crucial to characterizing more complicated structures.

Commercialization of inkjet printing demands that the printed electronic components have physical properties no worse than those fabricated by traditional methods; for printed conductors, this means low electrical resistance and strong mechanical properties. Increasing the cross sectional area improves electric conductance, which permits a strong electric current to pass through with insignificant heat generation. On the other hand, there is always a tendency towards miniaturization in the electronic industry. For electrical circuits, narrow circuit conductors are always preferred. These two seemingly conflicting requirements of a larger cross sectional area and smaller width can only be resolved by increasing the thickness of the deposited film. Unfortunately, inkjet printing requires a low viscosity fluid ink to generate droplets smoothly through a 10~60 micron orifice. Once deposited on a substrate, the thin ink has a tendency to spread on the surface and the direct consequence is that the inkjet printed traces have a thickness-to-width ratio less than 1/50. Subsequent decomposition, evaporation and sintering will further shrink the material and decrease the thickness. Thus, the limitation in producing thick films is one of the biggest challenges for the commercialization for inkjet printed electrical components.

Thick films can be produced as electric circuits with the screen-printing method. For example, the screen printed conductor is characterized with thickness of 50 micron and 1mm width. The ratio of thickness to width is 1/20, larger than the ratio for inkjet printed conductors. Considering two traces of the same width deposited with these two different methods, the electrical conductance per unit length of the screen printed circuits could be much higher than that of the inkjet printed circuits, even if the conductivity was optimized close to that of bulk silver (1.6E-8 ohm.m). Multi-layer printing can help increase the thickness but will also adversely affect the material deposition efficiency. Formulation is especially important in increasing the deposition thickness, which has two-fold significance: first, surface tension and viscosity can be adjusted to avoid over-spreading on substrate; second, increase metal percentage for small shrinkage during curing. Substantial research in this area will be discussed later to increase the film thickness of inkjet printed components for the successful commercialization in multiple fields of industry.

2.2.2.3 Porosity

Pores are an inherent feature of sintering deposited conductive inks. They are present in the compact powder as inter-particle voids, forming a three-dimensional network. Consolidation increases the density and reduces the pore size, and thereby increases the strength and conductivity. Point counting with micrographs is an easy method for measuring porosity. It relies on the ratio of points on a grid falling on pores of magnified structure to estimate the fractional porosity. Electrical conductivities of metallic structures are deteriorated by the presence of pores. The ratio of the conductivity of a porous material to the conductivity of a bulk material k/k$_o$ is expressed as a function of the fractional porosity V_p [20]:

$$k / k_o = \frac{1 - V_p}{1 + 11 V_p{}^2}$$

The relationship between the conductivity ratio and fractional porosity is illustrated in Figure 5.

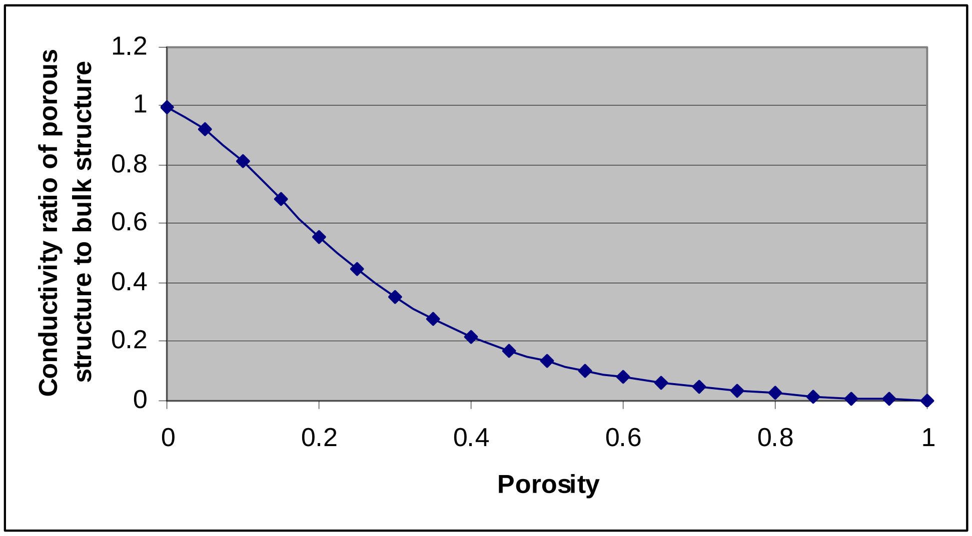

Figure 5: Electrical conductivity vs. porosity in sintering structures.

Porosity also affects the strength negatively by reducing the effective cross-sectional area. As pore shape becomes irregular, sintered materials exhibit decreasing strength. Small uniformly distributed spherical pores are proffered if porosity can be kept constant.

The elimination of pores will contribute to high strength and fracture resistant properties. The relationship for strength is approximately expressed as follows: $\sigma = \sigma_o K V_s{}^m$, where σ is the strength; σ_o is the strength of the bulk material; K is the stress concentration factor related to the geometric and processing constants; m gives the exponential dependence on density, and varies from 3 to 6; and V_s is the fractional density.

2.2.3 Functional properties of deposited conductors

2.2.3.1 Electrical resistivity

A simple resistance measurement consists of measuring resistance using an ohmmeter of a printed film of a given length and width. The electrical properties of a printed structure are affected by the homogeneity of the ink's chemical and physical properties, the structure geometry (thickness, edge definition, surface morphology, etc) and the interfacial properties at the interface between different materials.

2.2.3.2 Wear resistance

Rub resistance reflects the structural integrity of a printed surface during its useful lifetime. While printed electronics will likely be treated with much care, consumers have demonstrated that a certain amount of robustness will be necessary for successful commercialization of products. Some applications of printed circuits, for example, an automobile windshield heater grid, may face occasional scratching by things such as keys. Robust adhesion to glass is necessary to ensure the heat grids can still work with casual misusage. Quantification of rub is usually accomplished by mechanically abrading the surface using another representative surface, which would be encountered in a stack of printed matter shifting back and forth during shipment.

Adhesion describes the physical strength of printed ink structures on a substrate. Some testing methods simply require well characterized adhesive films (peel test) while others attempt to test this phenomenon using tensile testing devices.

2.3 CURRENT CONDUCTIVE INKS

To satisfy the requirements of inkjet printing, the inks must contain the appropriate precursors and carrier components. 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 and electrical conductivity [21]. We must seek to gain insight into the types of chemicals and chemical bonding that exists within a material [16]. Naturally, knowledge of the intrinsic properties of the various materials in a functional ink can be used to make an ink formulation more robust. Also, the chemical compatibility of different components in the functional ink formulation may alter the electrical properties of the functional ink, therefore, it is critical to understand the chemical interaction between every component to ensure optimal functional ink electrical performance.

There are several categories for the main ingredients of conductive inks, which include nanoparticles, microparticles, and metal organic decompositions. These conductive inks are just briefly sketched here. Detailed information and discussions concerning these inks are discussed in the next three chapters, which are titled as ‘Conductive inks with particles suspension’, ‘Formulation of a novel aqueous solution of conductive ink’, and ‘Metallo-organic decomposition inks', respectively. In the final chapters, some general conceptions considering formulation and post-processing of inkjet printing conductive traces are discussed.

2.3.1 Nanoparticles

Nanoparticles typically measure 1 to 100 nm in diameter and consist of atom clusters. Because of their very small size, nanoparticles exhibit melting temperatures as low as 1000^{o}C below their bulk material [22]. 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 energy. 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 or 60 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 gold particles that are 10% by weight in alpha-terpineol into a colloid [5]. MEMS and electric circuits were reported to be inkjet printed with nanoparticle conductive inks. When sintered at 300^{o}C for 10 minutes, the conductivity of the nanoparticles slowly increased over time. 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). The limited conductivity is probably the results of organic solvent inclusions in the metal and/or incomplete sintering of the particles. 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 [4][23].

The plastic-compatible conductive ink was inkjet printed onto polyester substrate at room temperature with a curing temperature under 200^{o}C with sheet resistance as low as 0.03 ohms/Square in 1μm thick films.

2.3.2 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 the metallo-organic compound decomposition during curing. In the process, gaseous byproducts of the decomposition leave the system, providing contamination-free metal films. Computer controlled inkjet 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 [24]. 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 a reduction process. The National Renewable Energy Laboratory reported the inkjet printing of metal organic decomposition (MOD) inks that had good adhesion and low contact resistance [25-26].

2.3.3 Micro-scale metal particles ink

The use of conductive paste based on metal particles is a mature technology and commercialized with the development of the electronic industry. Some examples of utilization can be found in membrane switches, printed circuit boards, medical sensors, telephone equipment, printed switches, computer housings, heating elements and the like. This ink generally consists of a dispersion of metal or carbon particles and synthetic resins in organic solvents. Metal particles of copper, nickel, silver or silver-plated copper are normally used. There are abundant resources about the formulation of the conductive paste from the vendors' manuals or patents. Herein, a novel conception of 'chemical welding' micro silver flakes was introduced, which may represent the technology tendency in this specified field. The formulation was disclosed of a conductive ink formed of a mixture of metal flakes and metallo-organic decomposition (MOD) compounds in an organic liquid vehicle [27-28]. 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 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 colloidal silver with a mean particle diameter of approximately 20 nanometers, the temperature for consolidating the metal has been further reduced to 270°C. Heating the deposited material to temperatures just above 300°C results in consolidated material with electrical resistivity of around twice that of the bulk metal and with good mechanical properties. Unfortunately, the micro-scale metal particle ink is too thick to be inkjet printed in the investigator's preliminary experiments.

2.3.4 Aqueous solution of silver inorganic compound

Nano scale particles or MOD precursors are two general resources for synthesizing conductive inks and their rheological properties permit inkjet printing. They work well under small scale experimental conditions, but resources are expensive and sometimes even not available commercially. In the current research, the investigator has developed a novel aqueous ink composition for CIJ printing that is being patented by the University of Pittsburgh. The main precursor should be a commercially available compound that is much less expensive than metallo-organic compounds and nanoparticles colloids. Due to the low cost, silver nitrate (chemical formulation as $AgNO_3$) was first 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 100g 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.

3.0 CONDUCTIVE INKS WITH PARTICLE SUSPENSION

3.1 NANO-PARTICLE COLLOID INKS

3.1.1 Size effects on melting points of nanoparticles

As mentioned previously, nanoparticle inks contain metallic particles that are extremely small within 1~100nm range, a collection of about 100 atoms. Nanoparticles can not be observed with the naked eye; the ultra fine particles that are visible to the naked eye are in fact coagulated nanoparticles. When heated up to the temperatures far below the melting points of bulk material, the nanoscale metal particles essentially weld themselves together, forming a highly conductive ink. Size effect on the melting points of tiny particles is the main theoretical basis for nanoparticle ink, as discussed in the following.

Using a scanning electron-diffraction technology, small particles have been shown to have a melting temperature which depends on the particle size [22][29]. The observational methods for defining melting include: Disappearance of the state of order in the material; Modification of the rate of evaporation at the melting points; Modification of the particle shape at the melting point. Gold was extensively researched because first of all, gold has a very weak affinity for oxygen, and second, the vapor pressure of gold remains relatively low up to the melting point. Specific to the papers are gold nanosized particles (2-4nm diameter), which possess drastically lower melting temperature (approx 300-400°C) compared to the melting temperature of bulk gold (1063°C).

Pawlow improved the Gibbs-Thompson model by considering the equilibrium of a liquid spherical drop with both a solid spherical particle of the same material and its vapor. This model leads to the following well-known equation:

$$\frac{T_\infty - T}{T_\infty} = \frac{2}{\rho_s L_{sv} R_s}\left[\gamma_{sv} - \gamma_{lv}(\frac{\rho_s}{\rho_l})^{2/3}\right],$$

where ρ_s is the density of the solid phase

ρ_l is the density of the liquid phase

L_{sv} is the latent heat for the solid-vapor phase transition

R_s is the radius of the sphere solid region

γ_{sv} is the solid vapor interfacial energy

γ_{lv} is the liquid –vapor interfacial energy

T_∞ is the bulk melting temperature

T is the small particle melting temperature.

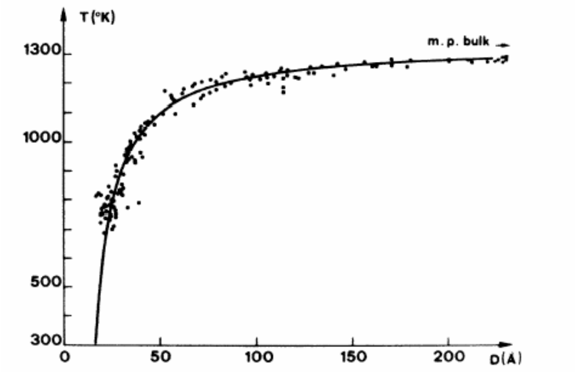

Figure 6: Size effects on the melting points of gold particles.

A theoretical quantitative explanation of these results was found in several ways: some studies are based on phenomenological thermodynamics, some others upon statistical mechanics or computer simulation. The difficulties lie in the choice of a phenomenological model and in the choice of a particular fusion criterion. The Pawlow theory was found to predict too high melting temperatures for the small size of bulk gold by subsequent researchers.

It is worth mentioning that for the special case of sintering metal particles into dense films, absolute melting phenomenon is not required. According to sintering theory and practice [20], to form dense solid structures, powders can be sintered not only in complete liquid-state, but also in partial liquid state and even in solid state. Consequently, it is not surprising in practice that continuous gold films are formed by heating 2-4nm nano-gold colloid at only 150^{o}C, which is even far below the predicted melting points of 300^{o}C from Pawlow theory (see Figure 6).

3.1.2 Synthesis of nanoparticles with physical or chemical method

Nano-scale metal particles can be produced by chemical synthesis or by physical processes. As a physical method, the gas evaporation method (GEM) is essentially a process of evaporation and condensation in inert gas atmosphere (Figure 7). This is analogous to water evaporating from a hot surface and condensing onto a cold surface to form tiny droplets. There are several heat sources for the evaporation process such as arc, laser and resistance heating. Studies have shown that induction heating is appropriate for making a large amount of nanoparticles with uniform particle size. The collection of isolated single particles should be treated with special care to avoid extra growth of particle size.

GEM is specified with narrow particle size distribution and little contamination on the particle surface. The particles are produced under conditions of quasi-thermal equilibrium and have good crystallinity. The size of the particles can be controlled by adjusting the evaporation source temperature and the inert gas pressure. In the theory of the GEM method, any material that is evaporable can be made into nanoparticles. So GEM can be a general fabrication solution for metal nanoparticles and metal oxide nanoparticles. GEM is the possible fabrication method for most electrical materials for conductors, insulators and semiconductors. Another important feature is that the individually separated particles rather than aggregated particles are fabricated and the unique characteristics of separated nanoparticles can be preserved with GEM.

In the chemical synthesis, the metal compound is reduced to pure metal. To avoid the coagulation of fine particles, a spray of surfactants, such as phospholipids, sulfuric lipids and alkylthiolates is added. And these small surfactant molecules form shells on the reduced coagulate of atoms to avoid further particle growth. The capsulated particles are stable and soluble in an organic solvent. Chemical synthesis does not require special instruments such as vacuum pump for synthesis, but it is characterized with wide range of particle size. And the stabilizer on the particle may be an obstacle to have a contamination-free surface during curing and must be burn off at relatively low temperatures.

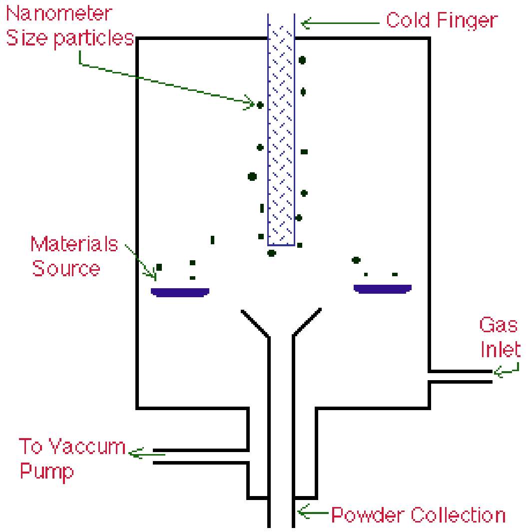

Figure 7: Schematic of gas condensation chamber for the synthesis of nanophase materials [30].

Standard circuit boards are generally fabricated from epoxy-fiberglass, phenolic fiber, or polyimide. A special requirement for inkjet printing on these flexible substrates is that the curing temperature must be lower than 150°C to 300°C, because such materials deform significantly or lose original physical properties if heated above this range. By optimizing both the size of the nanoparticle and the length of the molecule chain for encapsulation, it is possible to produce particles that can be annealed at really low temperatures (<150°C) to form continuous gold films. It has been realized through a two-step process, involving the sublimation of the surfactants, followed by the melting, coagulation, and immediate solidification of the gold nanoparticles to form continuous gold films. The surfactant burning off temperature was sometimes determined visually. For example, when hexanethiol was used as the surfactant, the elimination of hexanethiol is observed by a rapid transition of the film color from black to gold accompanied by a sublimation of the surfactant molecules in the form of a black smoke. Upon further curing, the film underwent a color transition from a dull golden color to a shiny gold.

A research group at University of California, Berkeley used a systematic study of the synthesis parameters to achieve low annealing temperatures while maintaining low film resistance [23]. Only the encapsulant alkanethiol chain length and particle diameter had a significant impact on the temperature at which conduction occurred. There is a tradeoff between stability and the anneal temperature due to the instability of thiols with short alkane chains. Optimization of the process reveals that 1.5nm gold nanoclusters encapsulated with hexanethiol have good stability and are suitable for use as printed conductors on plastic. The thiol/metal mole ratio is the critic parameter that will decide the nanoparticles size, and consequently the thiol sublimation temperature and nanoparticle coalescence temperature.

Table 3 shows the results of the annealing tests. From this table, it is apparent the required anneal temperature is a strong function of the encapsulate carbon chain length. It is also found that addition of three methylene units to the chain increased the resistivity by an order of magnitude, for example, 6 to 7 Ω cm for $C_6H_{14}S_2$; 80to 90 Ω cm for $C_9H_{20}S_2$; 1400 to 1600 Ω cm for $C_{12}H_{26}S_2$. By reducing the carbon chain length to four or six (Butanethiol or Hexanethiol respectively), it is possible to obtain nanocrystals that anneal at temperatures compatible with many low cost plastics.

The adhesion of the inkjet lines to the polyester was found to be a strong function of the temperature of the substrate during ink jetting. In general, it was found that adhesion improved dramatically when the temperature of the substrate was raised close to the thiol sublimation temperature. The reason for this improved adhesion is currently under investigation. It is suspected that some thiol remains as an interfacial layer between the plastic and the gold, improving the adhesion.

Table 3: Variation in transition temperatures during anneal as a function of encapsulant chain length and nanoparticle size [23]

	5nm particles		
Encapsulant	Thiol sublimation temperature	Au coalescence temperature	Conduction temperature
Dodecanethiol	170-180	170-180	170-180
Octanethiol	160-172	160-172	170
Hexanethiol	100	120	150
Butanethiol	120	120	120
	1.5nm particles		
Encapsulant	Thiol sublimation temperature	Au coalescence temperature	Conduction temperature
Dodecanethiol	190	190	190
Octanethiol	168-180	168-180	175
Hexanethiol	169	175	175
Butanethiol	127	127-137	133

3.1.3 Nano-gold ink

Brust et al. first reported the synthesis of thiol-derivatized gold nanoparticles in a two-phase liquid/liquid system [31] and later in a one-phase system [32]. In brief, metallic gold was produced by reduction of gold compound $HAuCl_4$. Hexanethiol was added during the reduction to encapsulate nano-size gold atom collections from further coagulation. It has been proven in the preliminary experiment that the dry nano-gold powders can be handled as simple organic compounds by following the reaction formulations and steps described as:

<u>Step 1</u>: 1.5 gram of tetroactylammonium bromide was dissolved in 80 ml of toluene and added to 0.31 g of $HAuCl_4$:xH_2O in 25 ml of deionized water. $AuCl_4^-$ was transferred from the aqueous solution into the toluene organic solution as the formulation shows. The transparent organic solution turns red.

$$AuCl_4^- + N(C_8H_{17})_4.\ (C_6H_5Me) \rightarrow N(C_8H_{17})_4.\ AuCl_4(C_6H_5Me)^-$$

<u>Step 2</u>: A calculated mole ratio of a hexanethiol was added to the gold solution, with the fluid turning yellow.

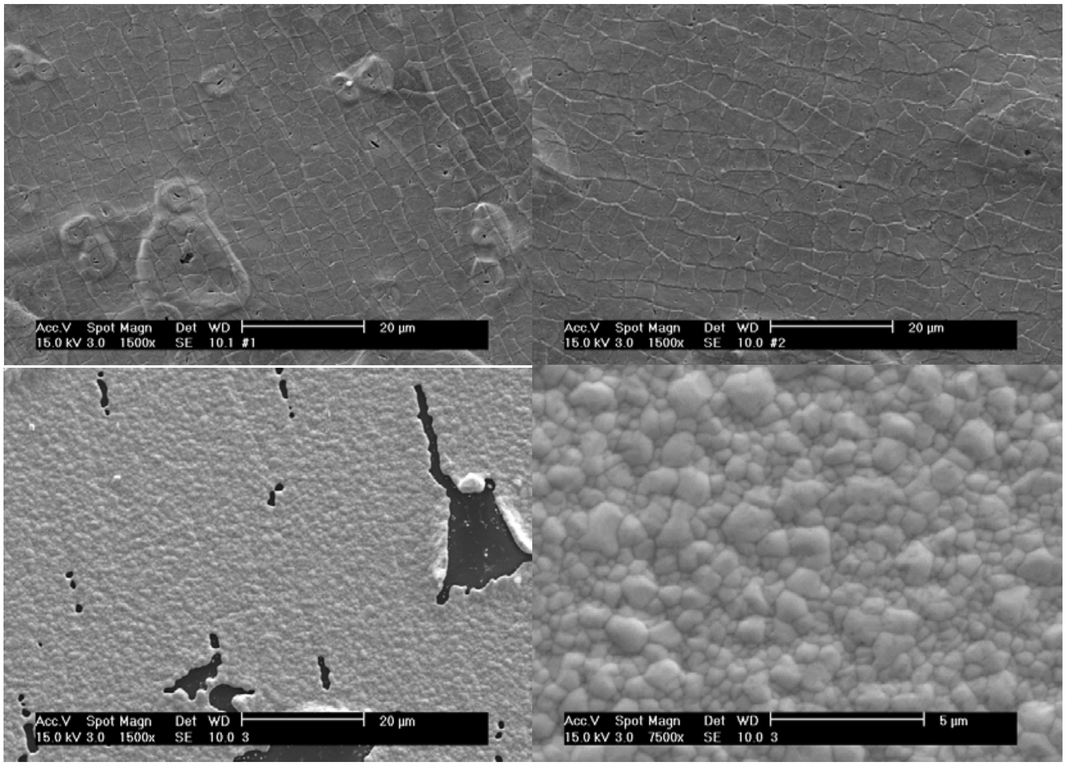

Figure 8: Substructures of metal film deposited with nano-gold ink on glass under different curing temperatures. a) Cured at 175°C for 15 minutes; b) 175°C for 15 minutes and then 400°C for 30 minutes; c) 175°C for 15 minutes and then 550°C for 30 minutes; d) the magnified crystal structure of c).

Step 3: Sodium borohydride aqueous solution was added into the organic phase with a fast addition over 5 minutes. With the addition of reducing agent, the mixture turns brown then finally black. The mixture reacted at room temperature for three and a half hours. The newly formed gold particles were encapsulated with thiol molecule from further coagulation.

$mAuCL_4(-)\ (C_6H_5Me) + n\ C_{12}H_{25}SH(C_6H_5Me) + 3m\ e(-) \rightarrow 4\ m\ Cl(-) + (Au)m(C_{12}H_{25}SH)n\ (C_6H_5Me)$

Step 4: Toluene was removed and the leftover black particles were suspended in ethanol. The particles were washed with water, ethanol and acetone and air dried, sequentially. The black nano-gold powders were dissolved in a minimum volume of toluene to form saturated colloid and were ready to be deposited as conductive ink.

The nanogold conductive ink was then deposited with the micropipetted on glass substrate and the solution got dry instantly in air. The black trace was heated to 175^{o}C for 15 minutes and converted to continuous golden conductor. The hexanethiol was burn off followed by sintering of nanogold particles to continuous gold films. Rectangular crystal patterns with parallel grain boundary were observed in the SEM photo (Figure 8a) taken from the sintered continuous gold film. Spot contamination on substrates formed bubbles during curing and caused adhesion problems at these sites. The electrical resistivity was measured to be 3.2E-8 ohm.m, twice that of bulk silver. Further annealing the gold film to 400^{o}C for 30 minutes did not change the original crystal patterns. Only after the samples were annealed at 550^{o}C for 30 minutes, new crystal structure similar to bulk metal were observed to seed and grow from the original rectangular crystals (Figure 8c and 8d). Fractures were observed to originate from the contamination spots where there are adhesion and strength issues. It is estimated that the fractures were originated from the sintering shrinkage at these ‘weak’ sites and expanded along the original crystal boundaries. The rub adherence test proved the unacceptable weak adhesion.

Uniform nano-ink deposition and adhesion promoter in the composition was expected to help the stronger adherence to the substrate.

The electrical conductivity of the conductor from 550°C spiking is close to that of bulk gold. The film thickness is measured as small as 0.3 microns, which put limitations on both of the electrical conductance and mechanical strength on the final conductive traces. The electrical resistance of a conductive sample is about 3 ohm per inch with a 1mm width. Multilayer printing is specifically recommended for nano-particle conductive inks for thick film and better electric conductance.

3.1.4 Nano-silver ink

Silver is the most conductive material under ambient atmosphere. It has abundant resources and much less expensive than gold. The current investigation is attempting to determine a convenient synthesis method to produce stable nano-silver colloids for conductive inks.

Numerous publications have been reviewed by the investigator to obtain a reliable process for nanosilver particles. A statistic analysis helped conclude that the generally used silver compound is $AgNO_3$ and next to it is Ag_2SO_4; and sometimes the use of $AgClO_4$. Sodium borohydride ($NaBH_4$) has been widely used as an efficient reducing agent for silver ions. Special precautions should be taken while dissolving $NaBH_4$ in water because it reacts violently with water, and hydrogen is produced.

A stabilizer or surfactant is critical for the success synthesis for uniform nano-scale particles as discussed previously. For conductive ink, surfactant chemicals must be burn off during the curing process. For printing on flexible substrates, it means the surfactant chemicals have low boiling temperatures. Alkanethiol with a short carbon chain length will satisfy this demand and is thus preferred.

There are other surfactants that work well. It was reported that stable concentrated aqueous dispersions of silver nanoparticles of a narrow size distribution were prepared by reducing silver nitrate solutions with ascorbic acid in the presence of Daxad 19 as a stabilizing agent. The latter has an excellent capability to prevent the aggregation of nanosize silver at high ionic strength and high concentration of pure metal [33]. Instead of the reduction method discussed so far, a simple method [34] is developed in which silver salts of fatty acids were decomposed at 250^{o}C under a nitrogen atmosphere to form fine particles surrounded by alkyl chains. The nanoparticles can be soluble in organic solvents such as toluene, benzene and hexane. When the solution was painted on the solid substrates and heated up to 210^{o}C, conductive metal film was successfully produced. It is described as a simple method to make metal coating on any substance, even plastics.

Careful comparison of these procedures leads to either a one-phase or a two-phase synthetic method [35] to be chosen for synthesizing nano-silver particles. In the one-phase synthesis, 0.1ml of dodecanethiol was added dropwise to 30 ml of 0.03 M silver nitrate in ethanol with vigorous stirring. To the resulting solution, 60 ml of a saturated $NaBH_4$ solution in ethanol was added dropwise and then after stirring for two hours, the solution was cooled in a refrigerator at -18C for 4h. Thereafter, the solution was dried with an aspirator, and the remaining brown fine powder was washed with toluene and other organic solvent to remove extra thiols.

In the two phase synthesis, 30ml of 0.03 M silver nitrate solution and 50 ml 0.05 hexadecanesulfonic acid in toluene were mixed together, and the organics phase was collected. Then 0.2ml of dodecanethiol was added dropwise with stirring, and subsequently 25ml 0.4 M aqueous NaBH4 solution was added for an hour. The organic phase was concentrated to 10ml solution, and then diluted in 200 ml ethanol. The solution was kept at -18C for 4 hours. Thereafter, the solution was then fried and the remaining brown powders were washed with toluene and ethanol and acetone several times. Also, ammonium neodecanoate can transfer a silver nitrate aqueous solution into toluene in the form of silver neodecanoate.

The size of silver clusters range from 4 nm to 13 nm, and 6 to 9 nm sized particles are obviously dominant. It is found that the nano-silver particles via one-phase method seem to be more homogeneously distributed than those prepared via the two-phase method.

Both of the one-phase and two-phase methods were tried many times in the current investigation. Precipitation of silver particles was observed when silver nitrate was reduced by $NaBH_4$. The synthesized black powder could not dissolve in toluene to make a stable solution. Hexanethiol could not securely encapsulate silver clusters as it worked on nano gold fabrication introduced in previous sections. The lack of a concentrated stable colloid of nano-silver has impeded the real world applications. That is probably the reason why nano colloid of gold, as a relatively inert metal, has been more intensely researcher even though it is more expensive than nano silver.

In the current research, commercial ultra fine silver powders used as the precursors of conductive inks. The 30nm silver black powder was dissolved in toluene to make a saturated solution of conductive inks. The ink was deposited on glass substrate and first cured at 300°C for 5 minutes. The color of the film changed from black to white with the toluene evaporation and particles coagulation. The microstructure of the low temperature sintered conductor was shown in Figure 9. It is a typical porous silver network with unit size about 2 microns. Apparently, the nano-silver particles were first coagulated into micro-scale ones. The enlarged micro-scale particles were interrelated with the neck sintering. The electrical resistivity is around 5 times of bulk silver. The bond of the conductor to glass substrate was weak.

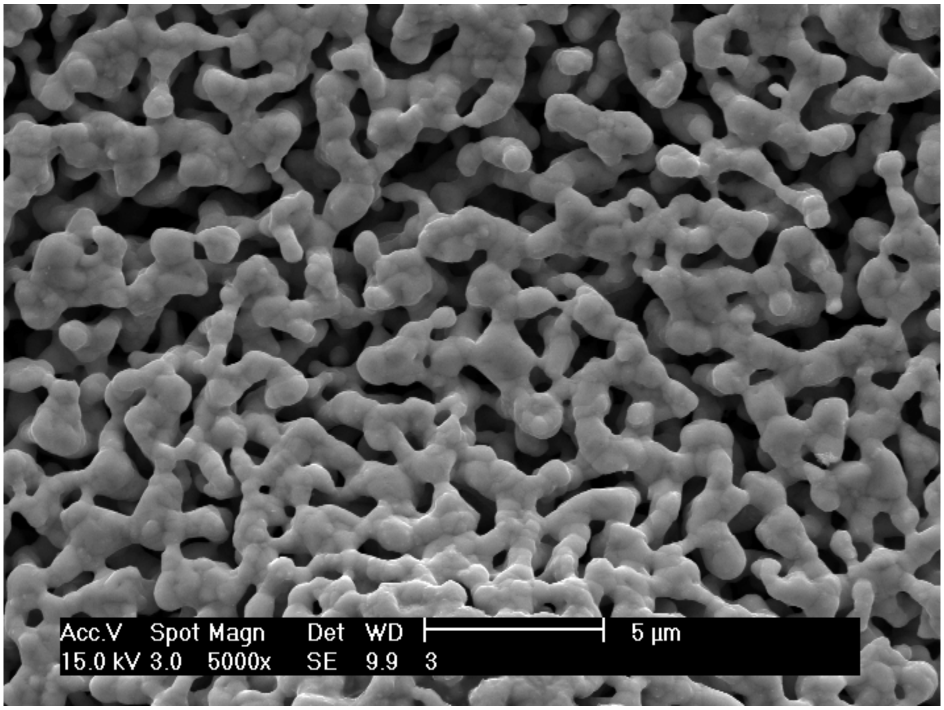

Figure 9: 30 nanometer silver particles sintered at 300°C for 5 minutes.

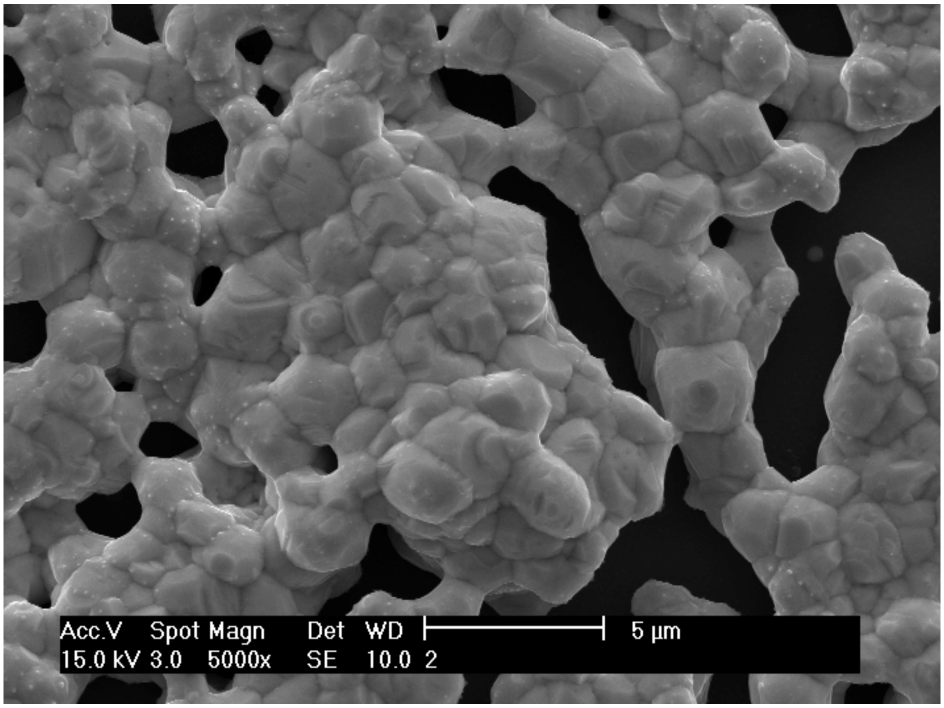

Figure 10: 30 nanometer silver particles sintered at 580°C for 30 minutes.

After being further annealed at 580°C for 30 minutes, the sponge structure in Figure 10 melted and formed closely-packed crystals similar to bulk silver. There is not sufficient silver to compensate for the shrinkage during sintering, so the sintered film is still in a porous state. But with the consolidated structure, the electrical resistivity was reduced to only twice that of bulk silver.

Another quantity of commercial 70nm silver nanoparticles was dissolved in toluene and then deposited on a glass substrate. After curing first at 300°C for 5 minutes, the SEM photo of Figure 11 shows that the nanoparticles were still in the original topography as deposited. Coagulating or sintering was not observed for the 70 nm nanosilver particles with curing under 300°C.

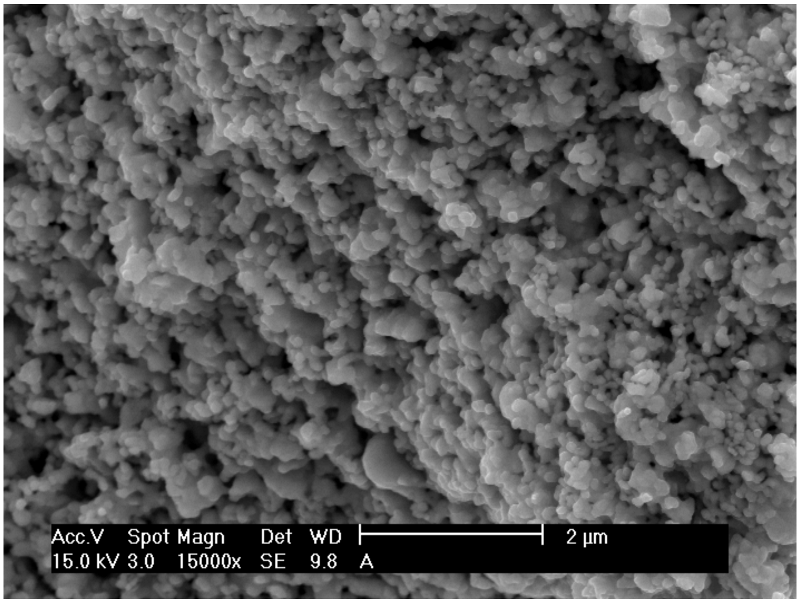

Figure 11: 70 nanometer silver particles sintered at 300°C for 5 minutes.

Further sintering of the 70nm silver particles (Figure 11) to 580°C for 30 minutes makes a miscellaneous structure as shown in Figure 12. Some nanosilver particles are coagulated into large micro-scale particles; but some are still in the original size. The electric conductance and mechanical adherence are not acceptable for the 580°C cured conductors. Comparing the different phenomenon of sintering nano-scale silver particles with variant sizes, the thermodynamic energy of nanoparticles for sintering was observed to match well with the tendency of size effects on melting points in Figure 6. The small particles can be sintered at relatively low temperature far below the melting points, while larger particles can only be sintered at higher temperatures. In the current case, 580°C of curing the 70nm silver particles could not complete the metallurgic stage that has been observed in 300°C curing for 30nm silver particles. The size of particles and the temperature are the most significant factors to determine if the consolidation can happen or not. The small size of particles is especially preferred for conductive inks.

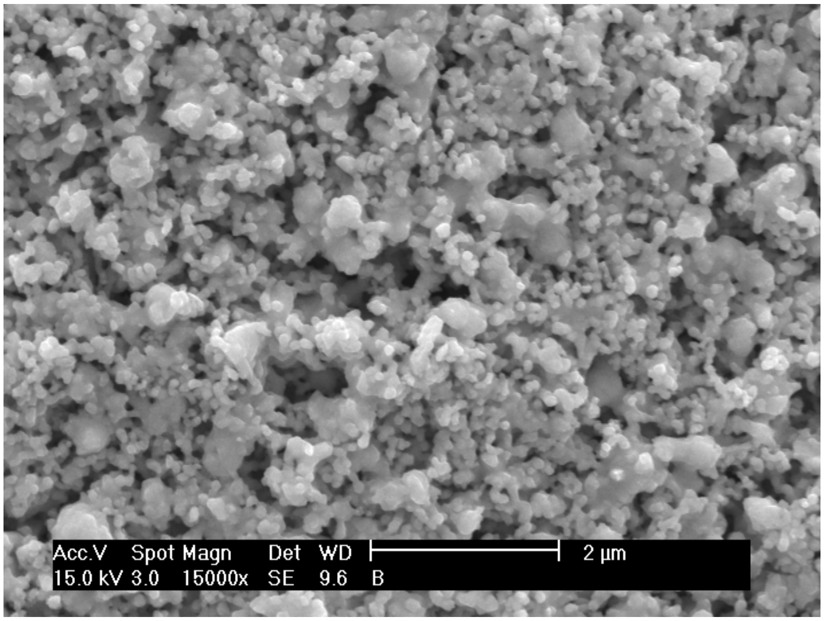

Figure 12: 70 nanometer silver particles sintered at 580°C for 30 minutes.

3.1.5 Summary

Nanoparticle silver or gold colloid was deposited as conductive ink in this chapter. For 1.5-5 nm nano-gold colloids, 175°C curing is sufficient to produce a continuous film on glass substrate. Compared with nano-gold, the chemical synthesis for nano-silver colloid was proven to be more difficult. Even the conductive inks made by dissolving commercial nano-silver powders in toluene are not stable and precipitation was observed in hours after a previous agitation. For 30nm nano-silver colloid, the required curing temperature is around 300°C while for 70 nm silver particles, it should be higher than 580°C or 580°C with much longer time. With the increase of particle size, a high temperature is required to sinter the separate particles into solid structures.

Both of the metal films produced from nano-silver or nano-gold have a weak adherence to glass substrate. Raising the curing temperature to 580°C for 30 minutes did not help. The consolidated metal films were closely packed and have a reasonable mechanical strength. But the film bonding to glass is weak because pure silver film cannot form molecular bond with glass that is composed of oxides. To increase the adherence, a certain adhesion promoter should be added to form an adherent interlayer to combine the noble metal films with the oxide substrate.

3.2 MICRO-PARTICLE SUSPENSION INKS

3.2.1 Introductory

Conductive pastes are defined as the material in paste state that can form electric conductor. The general composition for the conductive paste is micro-scale silver particles grilled with organic paste. After ambient atmospheric drying or some other forms of curing, the material shrinks and draws the conductive particle closer. The electric conductivity was realized from physical contact or electron hopping between neighboring particles. It has been found that a highly deformable, electric conductive ink can be prepared when the electrically conductive particles are in the form of flakes [36]. The plate-shaped flakes are preferably with a large flat surface and a small thickness no larger than two microns. In principle, it is advantageous to use flakes having a large surface area for lower temperature sintering and higher contact conductivity.

Up to now, the approach for producing conductive lines on glass substrates has involved glass frit for strong adherence. For example, U.S. Patent 5,141,798 discloses enamel for glass panes provided with silver conducting tracks that consist of 60-89.9wt% glass frit.

In general, conductive paste is designed for screen printing where the thick paste is squeezed through the masks to form a high density metal pattern. For inkjet conductive inks, there are great challenges because metal particles and glass frit will clog the inkjet orifice and are not stable in thin solvent. It is difficult to directly apply the conductive paste formulation for inkjet printing. However, micro-metal particle based conductive paste was discussed herein because the technology of conductive paste is fully developed and commercialized. The information on conductive paste is a useful guide for understanding the formulation mechanism of conductive inks.

3.2.2 A general micro-scale silver particles conductive paste

Several conductive pastes were purchased from different vendors. The general composition for conductive paste is micro-scale silver particles grilled with organic paste. There is not an essential difference in the formulation. A sample conductive commercial paste was deposited on a glass substrate and cured at 200^{o}C for 5 minutes as required by the application manual. The traces become conductive with the electric resistance of 11.2 ohm per inch for 1.5 mm width. The conductance of this paste is not very good and only applicable for short reconnection of broken electric circuits.

Observed from the SEM photo (Figure 13) of the previously mentioned conductive trace, thin silver flakes were loosely dispersed instead of being sintered together as shown for sintering the nano conductive inks. A binder was required to glue the flakes and push them together. As an insulator, this binder reduces conductivity and restricts the continuous electronic flow.

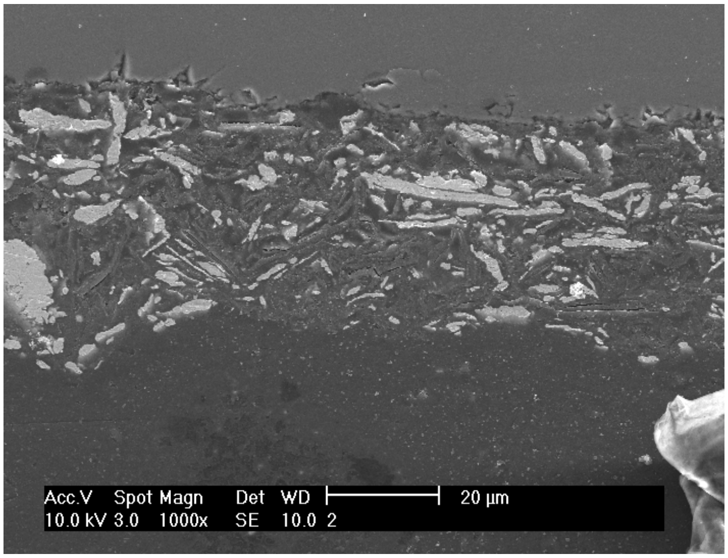

Figure 13: Conductive ink was cured at 200°C for 5 minutes.

Further annealing was attempted to increase the electrical conductance. Unlike that expected, the deposited traces lose the conductance completely during annealing at 500°C for 30 minutes (see table 4 below). It is also found that the conductance got impaired after a longer curing time (another 30 minutes curing at 200°C).

An SEM photo was taken to find the possible reasons of the conductivity loss under 500°C. The microstructures of the 500°C cured trace (Figure 14) are significantly different from the normal 200°C cured trace (Figure 13). In both photos, the white particles are silver, and the dark region is polymer matrix. The silver flakes in 200°C cured traces are uniformly distributed and interconnected with each other; while in the 500°C cured trace, the silver particles have aggregated and shrunk into chunks. The total surface area of aggregated chunks is significantly reduced considering that the original flakes have larger total surface area. The discontinuity of conductive metal particles leads to global non-conductivity. From Figure 13 and 14, it is worthwhile to notice that the deposited material grows into the glass substrate, which bonds the deposited material with the substrate. The adherence of the cured conductive paste to the glass substrate is strong.

Table 4: Effects of curing temperature on the sheet resistance of general micro-silver particle ink

	Sheet resistance Before curing at 500^{o}C	After curing at 500^{o}C for 30 min
Sample 1	0.94 ohm/square	Non-conductive
sample 2	0.76 ohm/square	Non-conductive
	Sheet resistance before curing at 200^{o}C	After curing at 200^{o}C for 30 min
Sample 3	1.1 ohm/square	1.46 ohm/square
sample 4	1.8 ohm/square	2.7 ohm/square

Note: “Before curing” is the state where the samples were cooled from curing in the stove of 200^{o}C for 5 min.

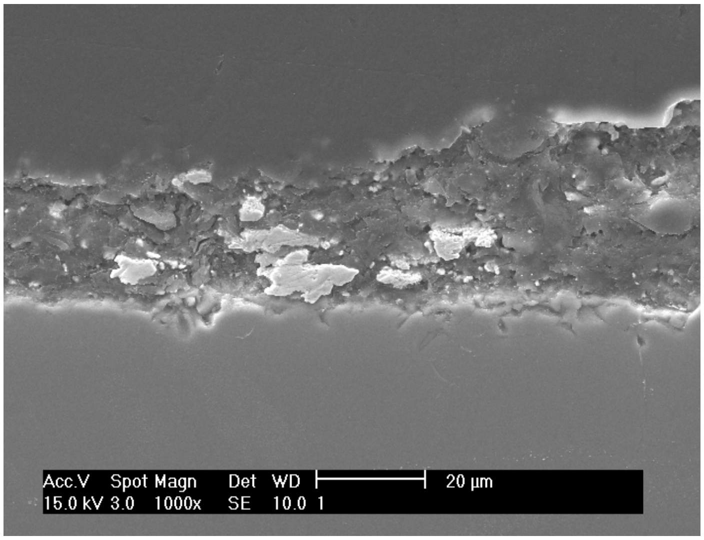

Figure 14: Conductive trace was cured at 500^{o}C for 30 minutes.

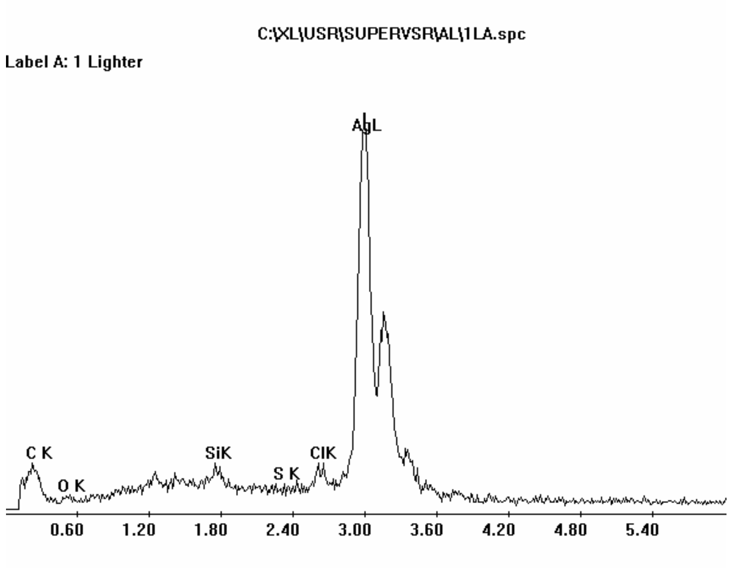

Figure 15: The composition of the silver particles on 500^{o}C cured trace.

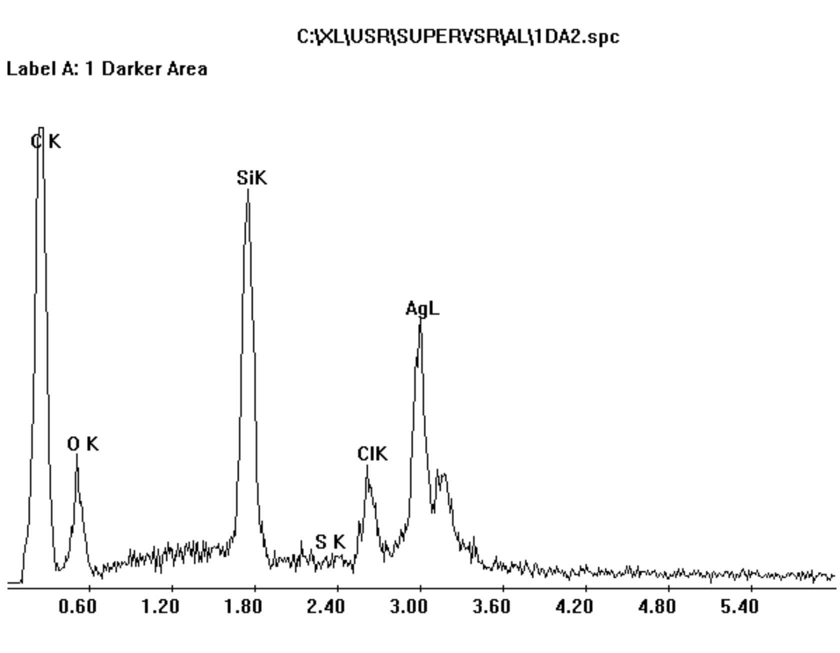

Figure 16: The composition of the dark matrix on 500^{o}C cured trace.

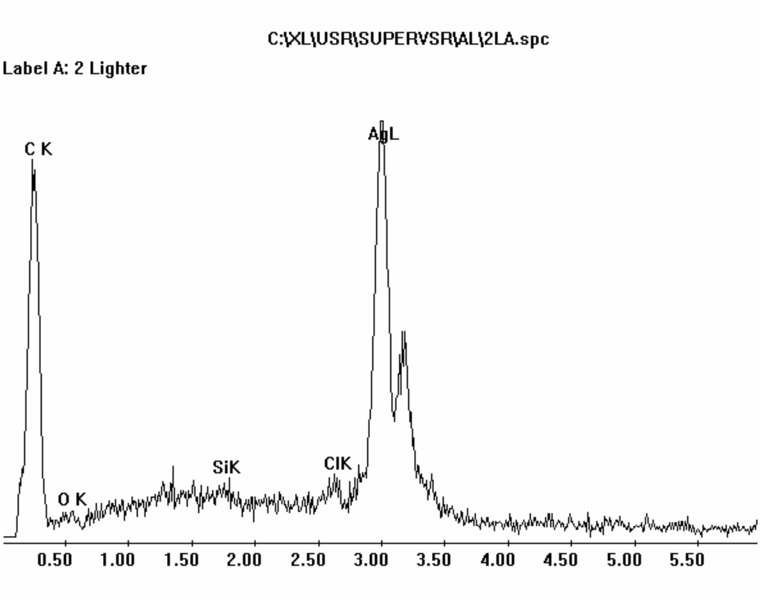

Figure 17: The composition of the silver particles on 200^{o}C cured trace.

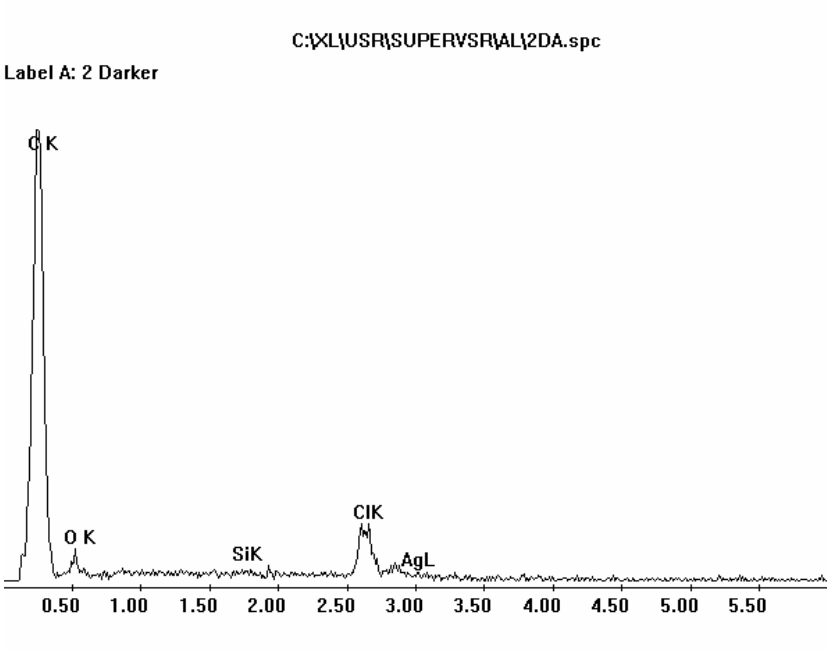

Figure 18: The composition of the dark of matrix on 200^{o}C cured trace.

Composition tests were further carried out on the samples cured at 500°C and 200°C respectively to find more useful information further explain the change in conductivity. Comparing the silver wt% in Figure 16 and 18 in the non-metal phase, the 500°C-cured traces have a higher concentration of silver than that of 200°C -cured traces. The polymer matrix of the 500°C trace has a higher concentration of silicon than that of 200°C traces. As exhibited in Figure in the metal particles, the 500°C-cured traces have a higher purity of silver than the 200°C cured trace. These changes during high temperature curing will help to understand the relationship between mass transfer and final properties. From the above analysis, it can be determined that during high temperature curing:

- Silver flakes aggregate into bigger ones to reduce surface energy;
- Some smaller particles are absorbed for growth of big particles;
- Some tiny particles melt and disperse into polymer matrix;
- Finally, the particles are pulled away from direct physical connections, the conductive units lost their continuity and the trace becomes insulator.

High temperature curing is proposed to melt or sinter silver particles to form a high density continuous film on the substrate surface. On the contrary, the deposited material loses its conductivity during the high temperature sintering. The required 200°C heating was presumed to evaporate extra organic solvent and shrink the matrix to pull the silver flakes closer. A simple surface contact between silver flakes is the designed mechanism for electric conductance. The consolidation was not expected and in fact it is hindered by the polymer matrix during the high temperature curing. For optimized continuous conductive silver film, the non-conductive material should be minimized in the composition, and is preferred to be evaporable during curing. In the next section, another novel micro-silver particle ink was designed to follow the principles of ink formulation. After 300^{o}C curing, the deposited paste was shown to produce a dense silver film for good electrical conductance and mechanical properties.

3.2.3 A miscellaneous conductive paste

A miscellaneous conductive ink was found to be composed of micro silver flakes as the main composition and does not contain polymer binder that impedes electrical conductivity. The ink was described in patent 6,036,889 with the composition of

- Silver flakes with the dimensional ratio of length to thickness between 5 and 50;
- Silver nanoparticles with dimension of about 10 to 40 nanometers; The colloidal metal constituents in the suspension can range from 10 to 50 wt%;
- Silver metalo-organic decomposition (MOD), it is silver neodecanoate in this case.

As discussed in the previous section, silver flake is the preferred form for highly conductive particles because of the larger contact area between silver flakes. In the current formulation of inks, the silver flakes contribute to electrical conductance, immobilization during melting and a skeleton for high thickness. The silver flakes also provide the surface area for chemical reactions of silver neodecanoate to decompose. Silver flakes dispersed in alpha-terpineol can be sintered to reasonably well-consolidated and produce a well bonded trace on polymer substrate.

Silver neodecanoate was added to change the rheological properties for a smooth paste. It begins to decompose at 200^{o}C to promote consolidation of the metal constituents and also promote bonding to the substrate. The decomposed metal atoms were accumulated on the silver flake surface, and then welded the silver flakes together at the temperature far below the melting points. This process is termed as ‘chemical welding’ to show the difference from general sintering in which surface energy is the main impulse.

Inclusion of an MOD compound is the most creative part of this invention. It is the first time silver flakes are consolidated through a process called ‘chemical welding’ contributed by the MOD compound. The other possible MOD compounds could be gold amine 2-ethyl hexanoate or platinum amine 2-ethyl hexanoate. Nanoparticles were added to further reduce the consolidation temperature from 300°C to 275°C, which is not as important as silver flakes and silver neodecanoate.

The miscellaneous conductive ink was pasted and then heated to 300°C, resulting in consolidation to a highly dense film with electric resistivity of less than twice that of the bulk metal and excellent mechanical properties. From the benefit of a low curing temperature for nano-silver particles and silver neodecanoate, the consolidated silver films (Figure 19) can be formed at a plastic compatible temperature with sufficient thickness of about eight microns. It can be determined from Figure 19 that there are two structures: big size flakes and small size MOD decomposition particles. A high electric conductance and strong mechanical strength are expected because the produced film is both dense and thick.

After a 275°C curing for 5~10 minutes, the deposited trace was measured to have electric resitivity of only 3.15E-8 ohm m, and 327°C curing, for 5~10 minutes can make 2.11E-8 ohm.m. For one antenna sample screen printed with this paste, which is 132 cm long, 0.75 mm wide, 10 μm thick, the electrical resistivity is 3.0E-8 and electric resistance of the total length is 5.5 ohm. The mechanical adherence is strong enough to pass tape test and ¾ pass crease. The comprehensive properties are attractive in many applications with the exception that the ink is too thick to be inkjet printed. The size of the flakes can be expected to clog the orifice. Thus, the current miscellaneous paste is suitable for screen printing instead of inkjet printing.

When silver flakes dispersed in alpha terpineol were separately deposited on a glass substrate to compare with the miscellaneous ink, observed in Figure 20, the 300°C cured substructure is uniformly distributed, an interconnected porous structure not as dense as that shown in Figure 19. It can be concluded that the miscellaneous ink can produce a more consolidated metal matrix with the addition of the MOD compound and nano-silver colloid. It is further illustrated that the addition of MOD and nano-silver to micro-silver flakes will greatly increase the density of cured conductors.

It is surprising to find that silver flakes can have metallurgical connected at a temperature of only 300°C, considering the melting temperature of bulk silver as high as 960°C. It is proposed that the tip of the flake has a high surface energy that initiates the neck sintering between flakes.

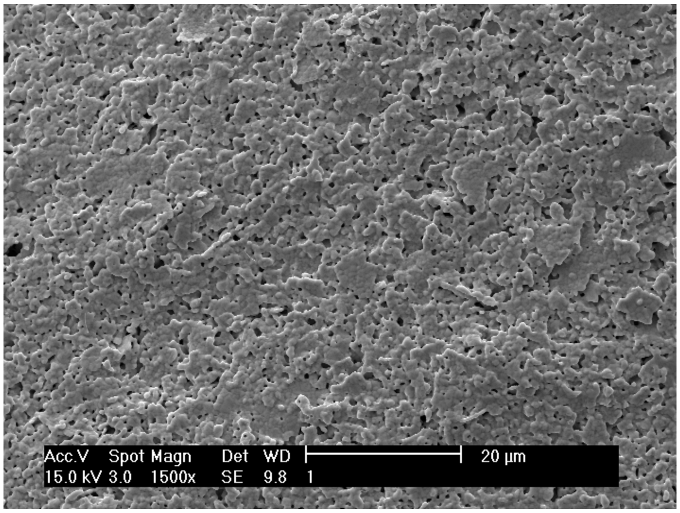

Figure 19: Conductive ink from mixture of Silver flake (8microns), silver metallo-organic compound and 30 nm silver particles; cured at 300°C for 20 minutes.

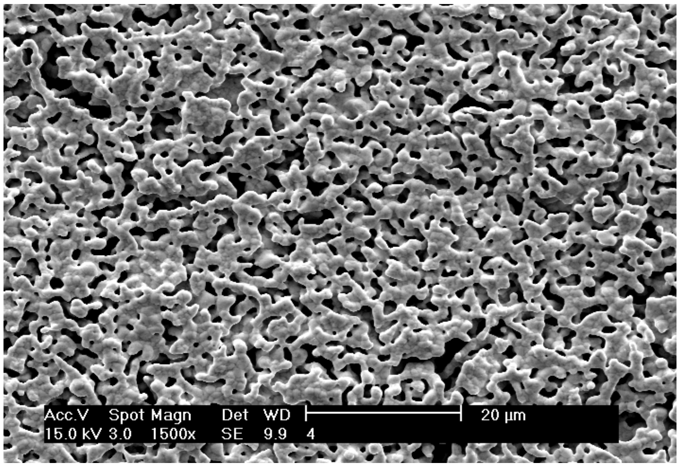

Figure 20: Silver flakes cured at 300^{o}C for 20 minutes.

3.2.4 Summary

In this chapter, the micro-scale silver particles inks were reviewed, tested and discussed. The mechanism to improve conductance and mechanical properties was well understood from comparing the general micro silver particle pastes and the novel miscellaneous paste. It can be summarized as:

- The general micro silver flake in organic matrix is not a good conductor. Avoiding non-conductive elements in formulation and increase the purity of cured metal film will improve the electric conductance; Choose evaporable materials or materials that can be chemically transferred into gaseous phase to leave the conductive phase;
- Porous structure or separated particles/flakes does not promote electron flow. Further annealing is necessary to consolidate the porous structure for better electrical properties;
- Increase the thickness for high electrical conductance, which is the biggest challenge for inkjet printed electronic components;

- Adhesion promoters are required in nano-scale or micro-scale particle inks; For example, in the miscellaneous conductive ink, a strong adhesion to glass substrate was found to be produced during decomposition of silver neodecanoate.

In general, nano colloid inks are suitable to be inkjet printed but limited by cost and a short shelf life. It can only be deposited with very limited thickness. Microscale silver particle paste is found to produce conductors with acceptable thickness, but is too viscous to be printed. All these problems suggest an investigation for particle-free solution conductive ink. In the following two chapters, the research will focus on solution inks without particles, which should satisfy the following characteristics:

- Stable solution with longer storage period;
- Abundant and inexpensive resources;
- No clogging at the orifice;
- Instant and convenient preparation;
- Improved adherence.

4.0 FORMULATION OF A NOVEL AQUEOUS SOLUTION OF CONDUCTIVE INK

Nano scale particles or MOD precursors are two general resources for synthesizing conductive inks whose rheological properties permit inkjet printing. They work well under small scale experimental conditions, but resources are generally expensive and sometimes not available commercially. In the current research, the investigator has 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.

Some soluble metal salts are reduced to a conductive metal state at high temperatures, which include metal salts of silver, gold, copper, etc. Noble metals can serve as thick-film conductors using air firing because these metals only slightly oxidize, if at all, and remain as electrical conductors when taken to high temperatures in the presence of oxygen. Other base metals lose their conductivity because of heavy oxidation if heated in ambient atmosphere [37]. Silver is a highly electrical conductor and free from oxidation at high temperatures. Therefore, the preferred noble metal salt for the conductive inkjet compositions is a silver salt, which includes the nitrate, lactate, or acetate. If these inorganic compounds can be determined to be suitable conductive ink with good thermal decomposition properties, there are many evident advantages over organic complexes, such as the ease of synthesis and handling, inexpensive, stable, non annoying smell, and dissolved in an aqueous solvent, etc. These characters are critical for the commercial application of inkjet printing of an electric circuit, and thus deserve testing.

Due to its low cost, silver nitrate was chosen as the primary inorganic compound in an aqueous ink composition. Silver nitrate has been used to produce metal silver films commercially for many years, for example, glass mirroring. 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. An interesting application was introduced that, by coating the carbon/carbon surfaces with molten AgNO3 at a temperature between the melting point of AgNO3 (212^{o}C) and the decomposition temperature of AgNO3 (441 ^{o}C), and then heating the resulting uniform coating of molten AgNO3 to about 700 ^{o}C, a uniform coating of silver metal has been formed [38]. Silver nitrate also has solubility of 219 g in 100g water, which is significant when a 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.

4.1 PRELIMINARY EXPERIMENTS AND THE OBSTACLES

Preliminary 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 Figure 21 was obtained. Unfortunately, there are problems with using silver nitrate alone in a conductive inkjet composition. The silver nitrate decomposition process can be violent and difficult to control. Furthermore, the silver metal film that is formed has poor adherence to a glass substrate.

As demonstrated by the figure, the trace was neither aesthetically appealing nor functional. After analysis, the white thick film in Figure 21 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 thin 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 electric conductor. The adherence of the solid spot to the glass substrate was such that it could be easily peeled off, further showing the inability of a simple silver nitrate solution to form a smooth continuous conductive trace. To overcome this problem of the inkjet composition contracting into separate spots after being printed onto a glass surface, water-soluble 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
e. Water soluble with high viscosity at low concentrations;
f. Decompose rapidly upon heating leaving no carbonaceous residues; and

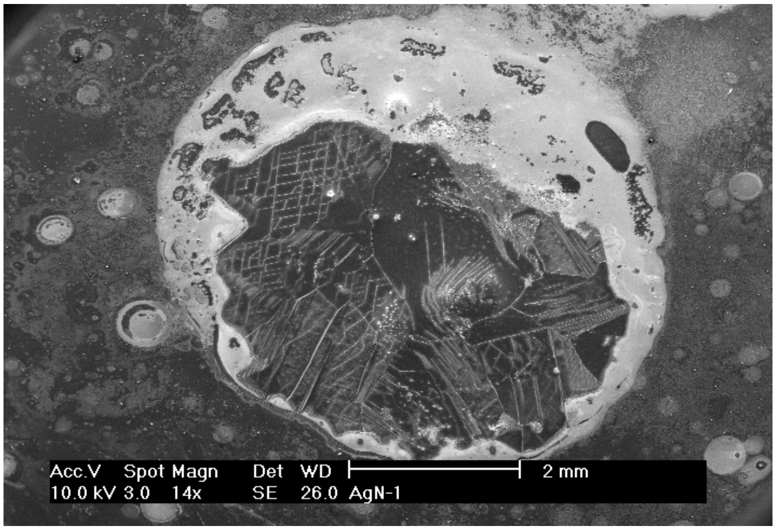

Figure 21: The SEM photo of decomposition debris after silver nitrate was thermal decomposed on glass slide.

A large volume of non-conductive residuals can substantially deteriorate the conductivity, which should be taken into consideration for selection of additives. One preferred additive is PVA. Additionally, U.S. Patent 50434451 discloses a PVA-based copolymer that can also be used in the conductive inkjet compositions. The disclosure describes a PVA-based copolymer having an average degree of polymerization of no more than 2000, preferably not more than 1000, and not less than 100, containing 20 to 90 mol%, preferably 40 to 90 mol%, of vinyl alcohol units, and containing 0.5 to 30 mol%, more preferably 2 to 20 mol%, most preferably 5 to 20 mol% of (meth)allyl group-containing nonionic monomer units or nitrogeneous-group containing nonionic monomer units. PVA forms an aqueous solution or slurry having an excessively high viscosity. The more nonionic monomer units the binder contains, the more readily the binder undergoes thermal decomposition.

Another water-soluble polymeric binder useful in the conductive inkjet compositions includes polyethylene oxide. Polyethylene oxide is a water-soluble binder that dissolves completely in water at room temperature. The molecular weight of the polyethylene oxide is preferably in the range of not lower than 100,000 and not higher than 2,000,000.

These large molecules such as PVA can make a clear and thicker aqueous solution silver nitrate. It has been shown by experiments that the reduction of silver nitrate can be slowed down to make a uniform smooth metal traces on glass substrate. The concentration of the water-soluble polymeric binder should be less than 10% by weight of the single valent metal weight. Higher concentration of large molecules of PVA makes the ink too thick to be inkjet printed. Furthermore, the residue from firing the polymeric additives will degrade the electric conductance because these residues are electrical insulators.

For this purpose, 0.5 gram of silver nitrate and 0.05 gram of PVA were dissolved in 1ml DI water to make the conductive ink for the following investigations. The ink was deposited on glass substrate and the fluid was viscous to avoid extending the width. The ink was cured at 500^{o}C for 20 minutes. The thermolysis went smoothly with a controllable rate to form a gray uniform trace. From the SEM photo of Figure 22 and 23, a highly porous structure was observed. The porosity was supposed to be caused by the gaseous phase evacuation from deposited solid phase.

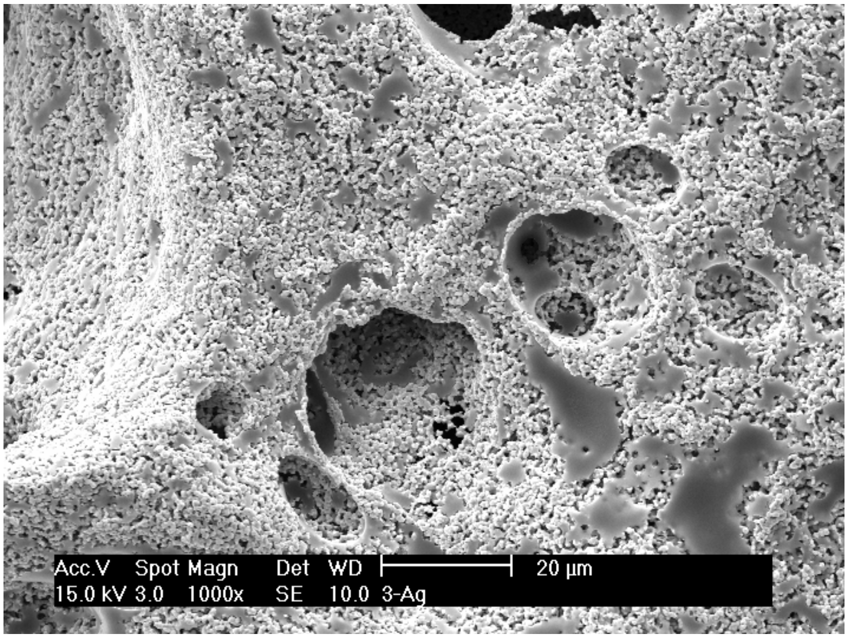

Figure 22: The silver construction of silver nitrate with PVA; cured at 500^{o}C for 20 min.

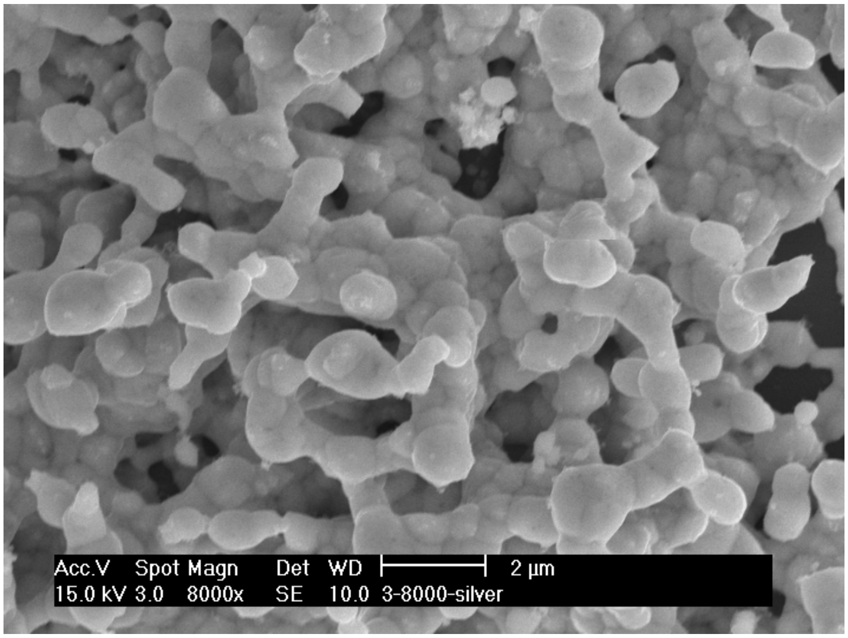

Figure 23: The porous structure from inks of silver nitrate with PVA; cured at 500^{o}C for 20 min.

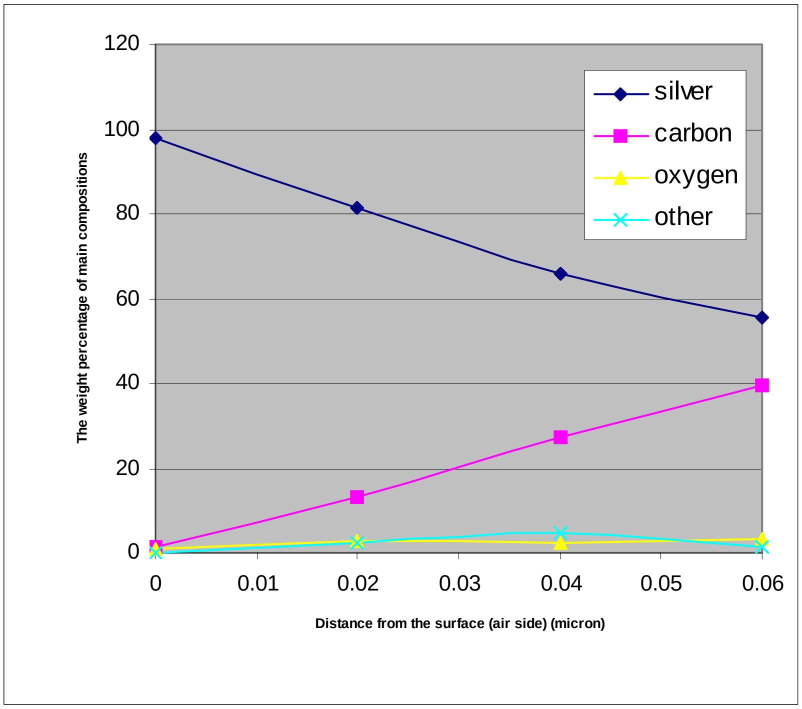

Figure 24: The weight percentage of main composition changes in printed conductor with the distance from the substrate.

From Figure 24, the results of composition test, the purity of silver is highest on the top of the deposited trace and decreases in the thickness direction from 98% to 56%; while carbon has the lowest weight contribution on the top surface and the highest near the glass interface. The average percentage of carbon is 22%, which means PVA was not completely evaporated from the solid phase. The silicon was not observed on the bottom conductor side near the glass substrate. It is an important phenomenon that there is no atomic bonding between the conductive trace and the glass substrate.

With the addition of the water-soluble polymeric binder of PVA, the resulting metal film after curing is a porous structure with fair electrical conductance and very low mechanical strength. The automobile windshield heater industry demands that the final conductor must resist 1000 cycles abrasion test with the ½ inch diameter steel ball loaded at 125 gram. The final conductors, with the addition of PVA, can be easily scratched off with a hard object and is absolutely not applicable.

As the traditional procedure accepted by glass industry, small particles of glass frit were tried as adhesion promoter. The current grill technology can produce glass frit in microns. Glass frit of 2~5 microns was added into silver nitrate water solution to the extent to make a temporary stable colloid; polymeric PVA was added as thickener to make homogeneous fluid. The mixture was inkjet printed on glass substrate. After curing at 500^{o}C for 30 minutes, the pale trace was found to have good conductance.

The mechanical adherence was tested with a pin-on-disk tribometer, the parameters are set up as below:

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

Photos were taken of the conductive traces where the steel ball glided through to compare the changes before and after the wear tests. In-time monitoring of electric resistance along both sides of cutting point during abrasion tests offered further information about the damage degree of conductive trace. The trace was cut off after only 300 cycles and the adherence was not satisfactory (Figure 25). The traces lost continuity completely, as determined by the in-time monitoring of electric resistance. From the above research data, it was found with inkjet printing method neither PVA nor glass frit can help silver nitrate aqueous ink with a strong adherence to the glass substrate as required by industries.

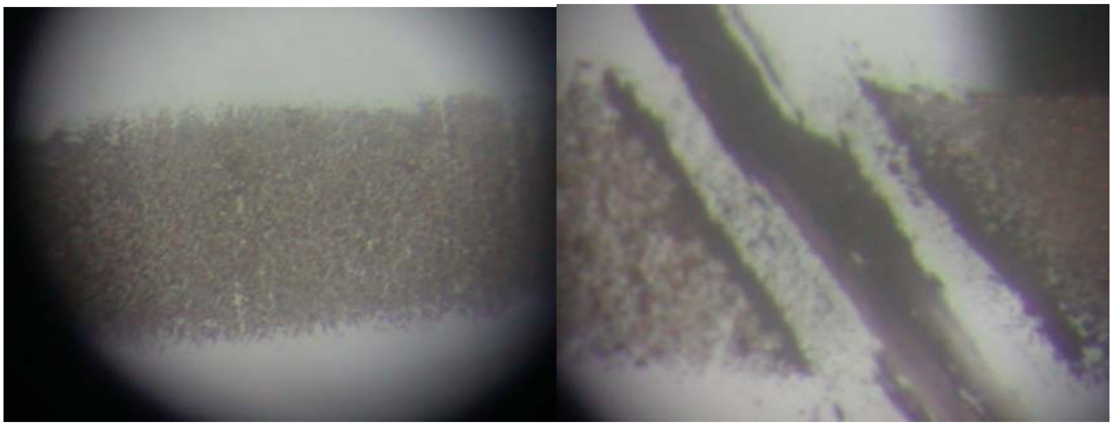

Figure 25: A typical continuous trace before wearing test (left) and after wear test (right).

4.2 ADDITIVES TO IMPROVE THE AQUEOUS SYSTEM

As mentioned previously, noble metals cannot produce solid bonding with metal-oxide based substrate such as glass, alumna or silica. It was confirmed by the investigator that gold or silver decomposed from their compounds cannot form a solid bond with glass/alumina/silica substrates while the base metal salt can provide improved adherence to the oxide type substrate. It is believed that the bass metal compounds are reduced in the form of metal oxide in an ambient atmosphere, and can serve as bonding to glass substrate, resulting in an excellent metal film adherence. For better electric conductivity, the molar concentration of the bass metal salt to the precious metal salt should be less that less than 20% and most preferably less than 5%.

To improve the properties of the silver nitrate solution, numerous base metal chemical additives were selected, tested, and compared based on their physical and thermodynamic properties in the solution together with the silver nitrate. Some additives were found to be effective in improving the conductive silver nitrate ink. The preferred multivalent metal salt for use in the conductive inkjet compositions is ($Al(NO_3)_3 \cdot 9H_2$). Aluminum nitrate nonahydrate melts at 73°C, dehydrates at 75°C, decomposes into basic salt at 135°C and completely decomposes into aluminum oxide and nitrogen gas around 500°C. In this manner, a viable conductive ink was produced by combining 25~100 gram of silver nitrate, 10~25 gram of aluminum nitrate nonahydrate and 100 ml of pure water into a transparent aqueous solution. The material was then deposited onto micro glass slides heated to 75^{o}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^{o}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 an oven that was preheated to 485^{o}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 26 shows an SEM structure of the conductive trace that was produced after curing. In the figure, there are many ‘cell-like’ composite 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 wear-resistant aluminum 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. Aluminum oxide is one of the most wear resistant and hardest materials and functions excellent as the adherence promoter. This special functional composite structure explains the beneficial characteristics of the trace.

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 not a clogging problem during the inkjet printing process after several days of continuous operation.

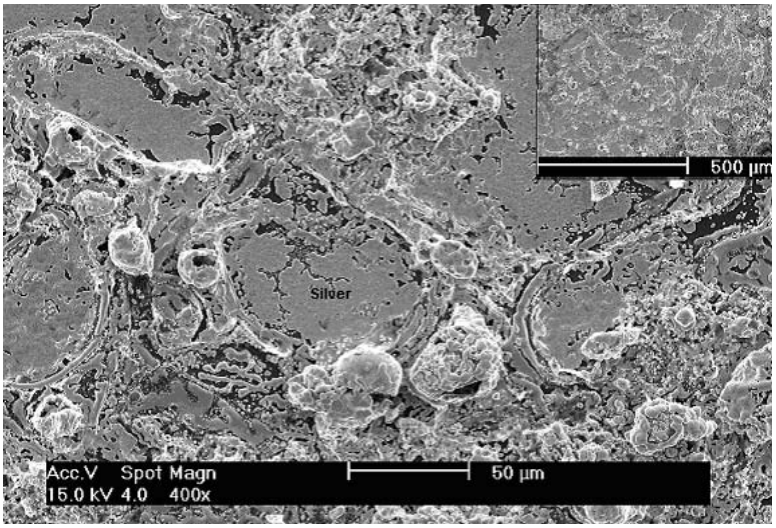

Figure 26: Microstructure of conductive trace after novel conductive ink was cured at 485°C for 20 minutes.

Table 5: 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

4.3 OPTIMIZATION

Once the preliminary ink solution was obtained, a factorial design was carried out to determine the critical processing parameters for optimizing the conductive inks. Electric resistance was the only outcome studied in the factorial design. Mechanical adherence of the ink was not considered because it was found to be a very stable property and closely correlated with the quality of the electric resistance. Three factors were screened:

Ink density: high (1.68 g/ml) and low (1.4 g/ml);

Substrate temperature: high 75°C and low 20°C.

Curing time and temperatures: high temperature at a short interval (550°C/5min) and low temperature at long interval (475°C/30 min).

It is clear from the factor design effects on sheet resistance in Figure 27 that all three of the factors - ink density, plate temperature and curing parameters - were important variables with analysis, curing temperature and ink density being relatively more important. Based on the factorial analysis, a dense ink with low substrate temperature, and low curing temperature was found to provide the best results when reducing electric sheet resistance. It is important to mention that a lower substrate temperature may not be practical in an industrial environment because the fluid state of the printed ink can spread on the substrate at low temperature and decrease resolution.

The response surface method was further investigated to find the optimum composition for the new ink. There were two additional factors studied: the amount of silver nitrate (ranging from 0.4~1.5 gram), and the amount of additive (ranging from 0.05~0.4 gram) material in 1ml water. Fourteen experiments were carried out based on a central composite design modeled in the MINITAB software. The electric resistivity was measured for each run and the data were input into MINITAB for optimization. From the response surface and the contour plot depicted in Figure 28-29, the electric resistivity was found to steadily decrease as the silver nitrate increases from 0.5 gram to 1.5 gram per milliliter of water. For additives, the Figure shows that there exists an optimum value around 0.2 gram in 1ml water on the bottom of the arc-shape. From the contour plot in Figure 29, 1.0 gram silver nitrate plus 0.2 gram additives was determined to be the best combination studied and worthy of further investigation.

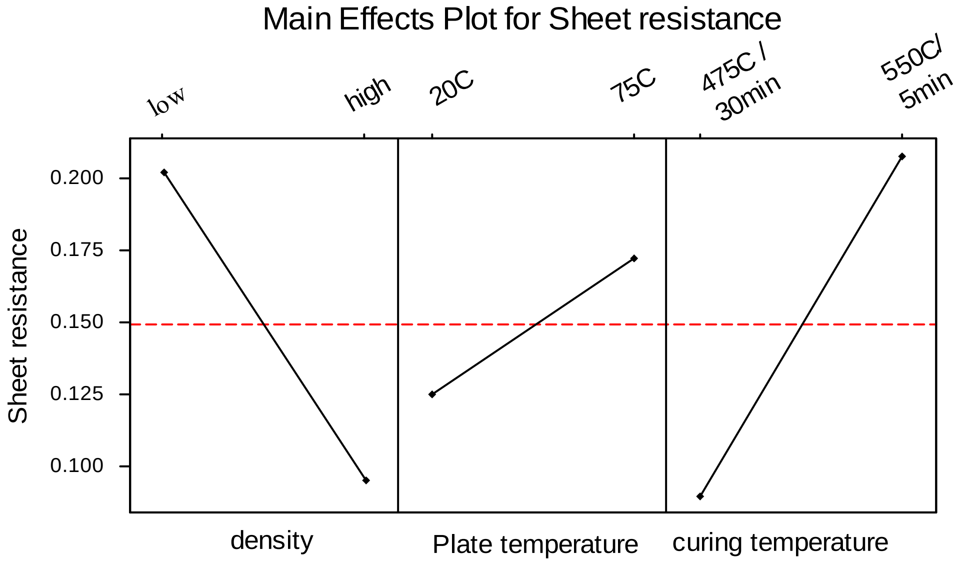

Figure 27: Factor design effects of sheet resistance on ink density, hot/cold plate, and curing temperatures, respectively, from left to right.

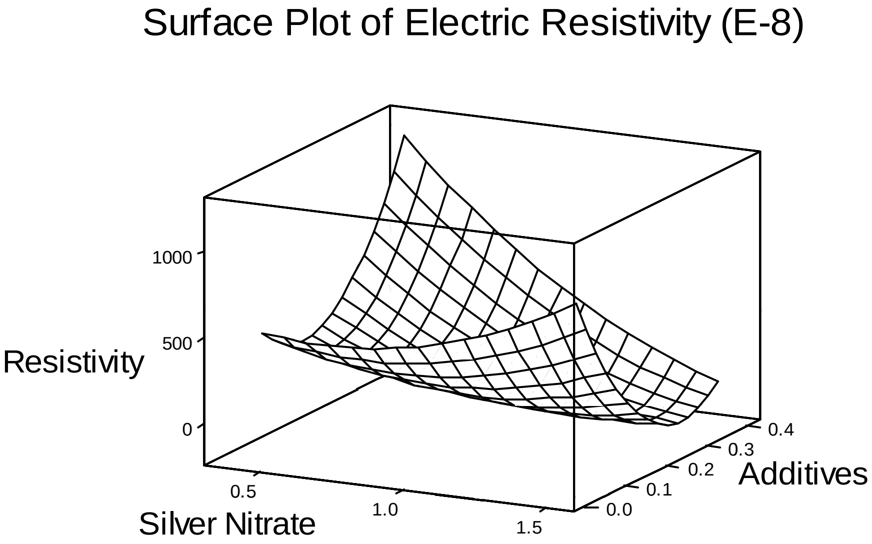

Figure 28: Response surface plot of electric resistivity on composition of silver nitrate and additives.

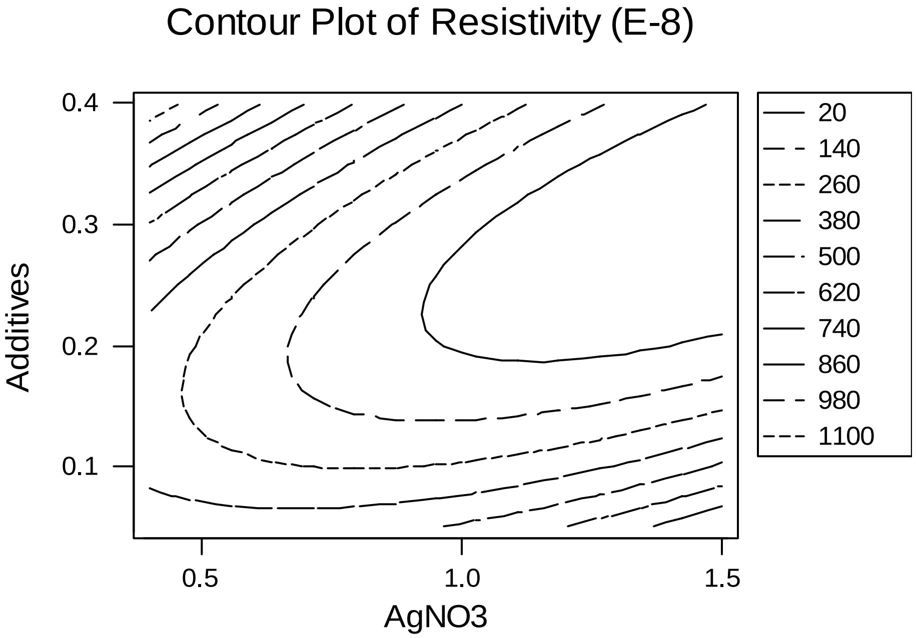

Figure 29: Contour plot of electric resistivity on composition of silver nitrate and additives.

4.4 ELECTRICAL AND MECHANICAL PROPERTIES OF FINAL CONDUCTOR

Utilizing the determined optimized ingredients of 0.2 gram of additives with 1.0 gram of silver nitrate in 1ml water, the crystals were sufficiently stirred until they 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.

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 as

$$\rho = \frac{R * w * t}{L} = \frac{0.5(ohm) * 1.3E-3(meter) * 1.8E-6(meter)}{25.4E-3(meter)} = 4.6E-8(ohm * meter)$$

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 (Figure 30). In-time monitoring of electric resistance along both sides of the cutting point during abrasion tests further confirmed the strong adherence of the conductive trace to the glass substrate (Figure 31). 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.

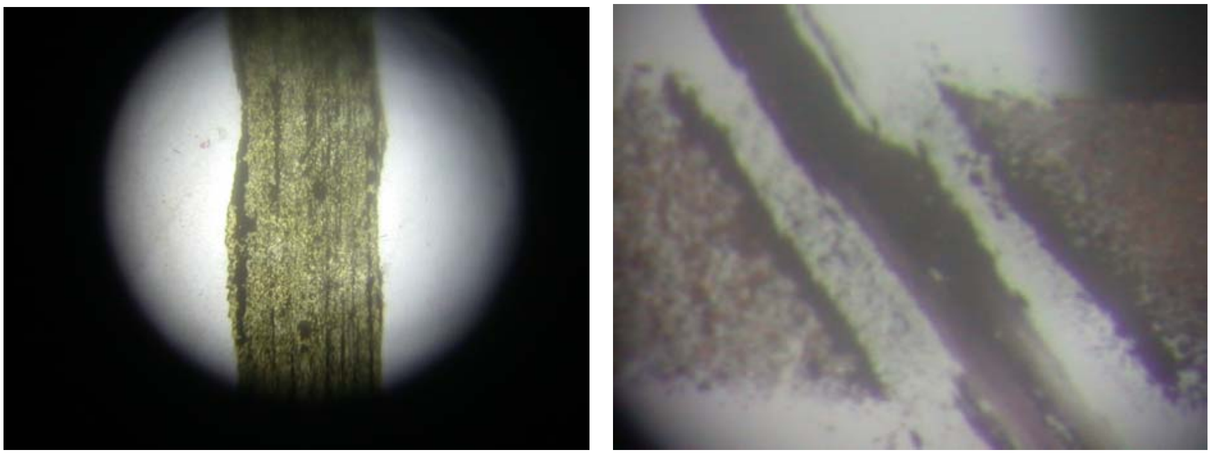

Figure 30: Abrasion was not observed on the conductor printed with current ink after 1000 runs (Left); Abrasion of the conductor with the ink printed using glass frit as adherence promoter after 300 runs (Right).

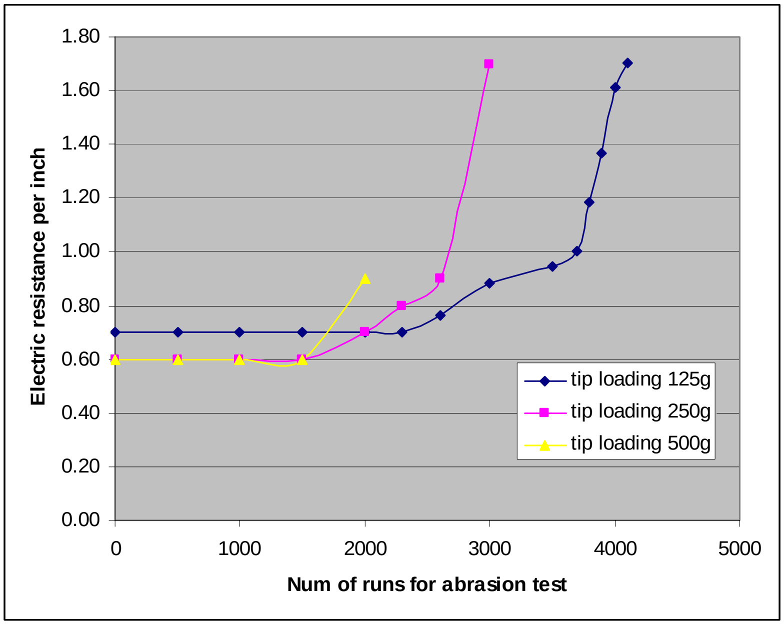

Figure 31: Electric resistance changes during 5000 runs of abrasion test, tip load: 125 g, 250g and 500g, respectively.

4.5 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:

a. A specified aqueous silver ink solution can be inkjet printed to produce conductive metal patterns that have satisfactory electric properties for use in commercial applications.

b. The most important ingredient in the aqueous ink is the silver compound, i.e. silver nitrate. Commercially available additives are required to make the silver nitrate a better conductive precursor. 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.

c. 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.

5.0 METALLO-ORGANIC DECOMPOSITION INKS

5.1 INTRODUCTORY

Although the literature on the deposition of metallic films from metallo-organic solutions spans over 100 years, and the technique has been practiced for centuries to decorate glass and ceramic tableware, it is only recently that MOD has been seriously investigated for electronic applications. In microelectronic technology, the shrinking size of integrated circuits and the need for ultra-fast interconnection metals have led to the intense study of organometallic compounds, especially metal compounds with a final product of pure metal with lower resistivities such as pure copper (1.67uΩ.cm) and perhaps pure silver (1.59 uΩ.cm). As introduced in the chapter of "Background of Conductive Inks", the MOD compound can be reduced to pure metal phase through thermolysis. Because metallo-organic based inks are true particle-free solutions, their rheological properties can be adjusted for a wide variety of application techniques. Such MOD inks have low viscosity, high metal contents, and suitable surface tension. The chance of clogging is minimized because there are no particles in the inks. All these features make MOD an appropriate precursor for inkjet printing inks. Since the deposited compound solution is at the molecular level, the atomic state of metal is formed immediately after decomposition. According to the size effects on melting points of tiny metal particles, it is practical to translate the decomposed ultra-fine metal particles into solid thin film on a substrate at relatively low curing temperature.

The critical factor in an MOD conductive ink is to select the right compound as the precursor. Most of the non-metal phases should leave the system through thermolysis and evaporation. The leftover metal phase should have high purity and high density, which ensure the high electric conductance and mechanical strength. Chemical precursors are designed so that chemical conversion to pure metal phase occurs at a sufficiently low temperature providing elimination of inorganic and organic ligands, also keeping in mind facile synthesis, environmental and health concerns and compatibility with other ink solution constituents. Other factors in consideration include solubility in various solvents, stability during the printing process, homogeneous film formation, adhesion to substrate, high metal content, and a long shelf life.

Vest investigated metallization of inkjet printed xylene solutions of soaps such as silver neodecanoate and gold amine 2-ethylhexanoate [39] on ceramic or silicon substrates. Preliminary experiments with silver neodecanoate demonstrated that well-bonded conductors could be produced on epoxy–glass circuit boards. Images of satisfactory resolution 75 microns were obtained, but the conductivity was low because of the extremely small thickness of the layers after decomposition which was less than a microns. A possible solution to this problem is to build up the thickness by printing for many layers, which Vest found suitable for fabricating silicon solar cells. Gold based metallo-organic materials were printed and dried at $125^{o}C$ for 10-20 min and then cured at $850^{o}C$ for 10 min [40]. For general thin film methods, improperly cleaned substrates or contaminants in a vacuum system can cause adhesion problems that are difficult to diagnose. MOD films, in contrast, which are fired at $850^{o}C$ in open air, have adhesion that is relatively insensitive to the condition of the substrate surface resulting in a more forgiving process.

Another similar field, called Chemistry Vapor Deposition (CVD), has been intensely researched for fabrication of electrical thin films. During CVD, precursor molecules are vaporized and transported into a reactor and then diffused to the substrate surface. The precursor on the substrate surface is then decomposed and incorporated into solid films. The byproduct is recombined through chemical reactions and desorbed into a gaseous phase.

Even though there are many similarities between CVD and MOD, there is a very significant difference between CVD and the investigated MOD method. The optimum CVD precursors prefer the complete volatility before the start of decomposition, while MOD precursors prohibit sublimation before the completion of decomposition. Many organometallic compounds will sublime during thermolysis, which places great obstacles in the selection of precursors for both CVD and MOD. The precious metal phase prefers to stay in the deposition system during the whole heating process. Most organometallic compounds are both air and moisture sensitive along with the added complications of their low thermal stability and light sensitivity. Thus the optimum MOD compounds to satisfy the conductive ink are few.

A broad survey of the potential utility of silver compounds as precursors for the formation of silver films [41-42] found them to be low melting point solids and volatile enough to be used for conventional thermal CVD, albeit mainly at reduced pressures. The results obtained suggest that the β-Ketoiminate complexes show greater potential, affording lower initial decomposition temperatures and somewhat higher deposition rates. The films produced are smoother, of good thickness with relatively low impurity levels combined with acceptable reflectivity. No impurities of oxygen, fluorine, phosphorus, or sulfur were detectable in the films. The films adhere well to glass or silicon as indicated by the adhesive tape test.

It has been shown that electric resistivities depend on the film morphology [43]. Laser CVD results are compared with a thermal CVD. The laser CVD results (with resistivities at the order of about $1e^{-6}$ ohm cm) were far better than the thermal ones (order of about $1e^{-3}$ ohm cm). The film morphology was finer and more distributed with a faster growth rate at much lower temperatures.

The deposition of silver on silicon through the reaction of AgF with the silicon surface is a feasible process [44].

$$Si + 4AgF \rightarrow 4Ag + SiF_4$$

A smooth film has been produced from temperature 80^oC to nearly 600^oC with the deposition pressure 10^{-6} Torr. The silicon-silver interface is etched during the deposition process, and this may contribute to the good adherence.

Most CVD precursor compounds are chosen from organometallic compounds, which consist of two parts: the central metal ion and the ligand. The metal and the ligand donate an electron pair to form a special type of covalent bond that can bind the organic or inorganic molecules to the central metal ion.

For metallo-organics (MOD), ligands are bound to the central metal ion through a hetero atom bridge. MOD compounds are pure synthetic metallic-organic compounds which decompose cleanly at low temperature to precipitate the metal as the metallic element or the oxide, depending on the metal and the atmosphere. The organic moiety is bonded to the metal through a hetero-atom providing a weak link that provides for easy decomposition at low temperature. Only metallo-organic compounds with heteroatoms of O, S, and N are considered to make MOD solution inks [45]. For most CVD compounds, direct carbon is directly bonded to the metal ion through a relatively strong link, which will not easily break to start thermolysis before completion of sublimation. Published literature suggests that metal salts of carboxylic acid, noble metal mercaptides, and complexes containing two different types of ligands are widely utilized in MOD.

5.2 AG(HFA)(COD)

Silver(hexafluoroacetylacetonate)(1,5-cyclooctadiene), also simplified as Ag(hfa)(COD) with molecular formulation $C_{13}H_{12}AgF_6O_2$, has been recently researched as a precursor of conductive ink by the National Renewable Energy Laboratory [25-26]. The compound was dissolved in an organic solvent such as toluene, ethanol or butanol, and then the solution was inkjet printed on a certain substrate with DOD technology. A silver film was formed upon solvent evaporation and decomposition at 300^{o}C, providing contamination-free metal films. The inkjet printed metal traces were reported as having good adhesion and measured a contact resistance of 400 $\mu\Omega.cm^2$.

To understand the MOD process and check the possibility of this compound as the precursor for the CIJ printing inks, preliminary experiments were carried out by the investigator. Ag(hfa)(COD) was dissolved in toluene with silver weight percentage of 15wt%. The solution has low viscosity thus suitable for inkjet printing. The ink was deposited on a glass substrate preheated to 100-150^{o}C. Toluene evaporates around 75^{o}C and the dark molten paste was left on the substrate. Further heating around 200^{o}C will begin the decomposition. The SEM photo of

Figure 32 shows that the metal silver particles with a size smaller than 100 microns were produced from the thermolysis of Ag(hfa)(COD). The decomposition is not complete because the composition test showed there is 9wt% carbon contribution on the surface of newly formed metal silver. With the gaseous phase evaporation, 'pores' were observed in the aggregations of silver particles.

Further curing at 350^{o}C for 20 minutes, thermolysis was completed with a highly porous structure shown in Figure 33 and 34. The silver has a high purity up to 95wt% (table 6). The silver particle aggregations were loosely dispersed on the glass instead of forming uniform continuous thin film. The small silver particles are not closely interconnected so that the deposited material has low electrical conductance and weak adherence to the substrate.

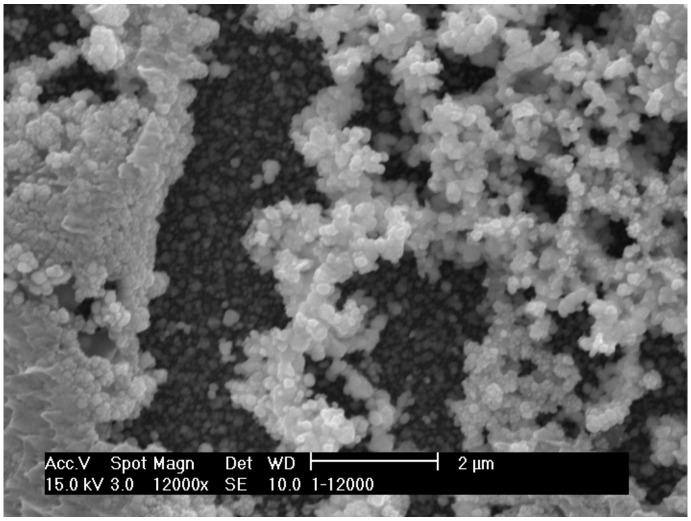

Figure 32: The micro structures of the silver in COD ink on 200^{o}C hot plate printing.

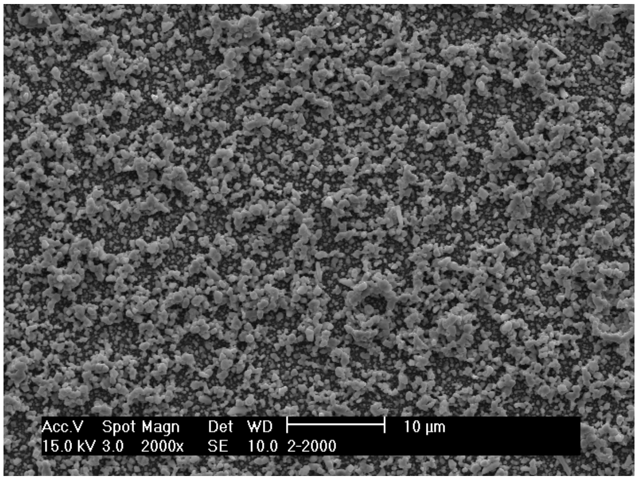

Figure 33: COD ink after 350^{o}C 20min curing; in toluene solution.

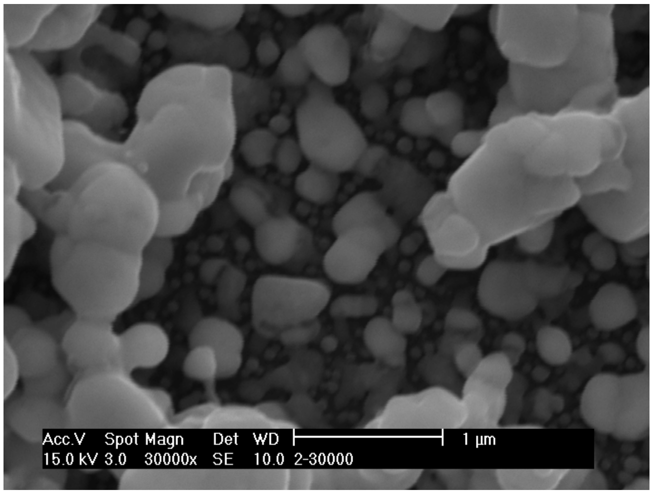

Figure 34: COD ink after 350^{o}C 20min curing, silver particles at high magnification.

Table 6: The composition of decomposed silver particles, cured at 150^{o}C and 350^{o}C respectively

	Wt% with 150^{o}C 20 min curing	Wt% with 350^{o}C 20 min curing
Carbon	8.59	3.52
Oxygen	2.25	0
Silicon	1.38	1.06
Silver	87.78	95.41

Preliminary experiments show that different solvents in which MOD precursors dissolve can change the morphology of metal film being patterned and consequently affect the properties. In this case, the investigator tested two MOD inks of Ag(hfa)(COD) in toluene and ethanol, respectively, keeping the same metal percentage of 15%. The two MOD inks were deposited on a glass substrate and cured at three different levels of temperatures: 200^{o}C, 300^{o}C and 450^{o}C. SEM photos were taken from these two inks cured at three different temperatures as shown in Figure 35 to 38.

Careful comparison of these two inks based on different solvents shows the ink with toluene as the solvent can deposit a more uniform film on a glass substrate (Figure 35); 200^{o}C curing produces denser silver particle with a smaller size (Figure 36); High temperature curing sinters the silver particle aggregations into 1-2 micron particles (Figure 37) and further integrates the particles into a network, which is more uniform and denser than the silver structure from the ethanol solvent (Figure 38). The toluene based solution ink was preferred for the high electrical conductance and mechanical properties.

Unfortunately, Ag(hfa)(COD) was proven to be unacceptable even though with toluene as the solvent; the electrical resistivity is several times higher than bulk silver; and the conductive trace can be easily scratched.

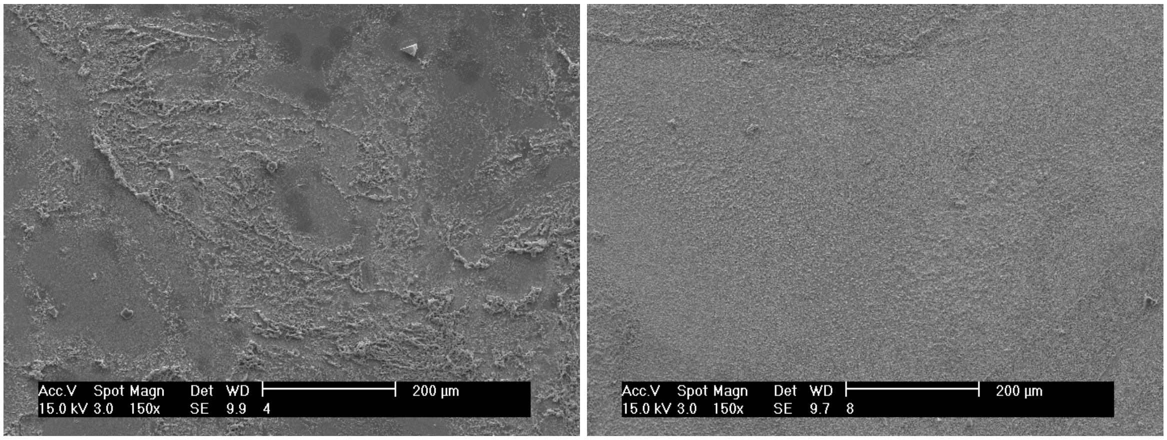

Figure 35: Profiles of deposited Ag(hfa)(COD) solution ink in different solvent, left: the non-uniform distribution with the ethanol solvent; right: The uniform deposition with toluene as the solvent.

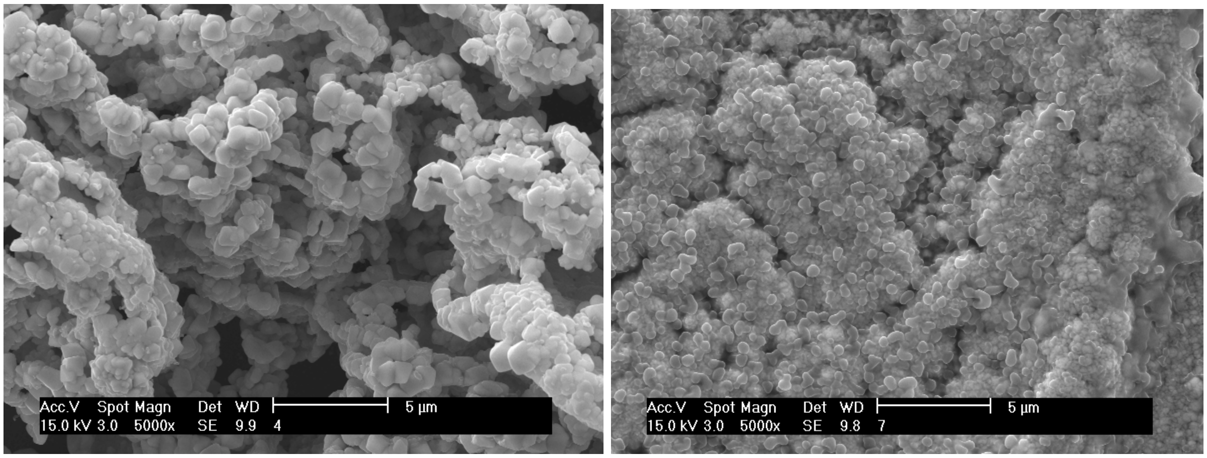

Figure 36: Solvent types affect the pattern of Ag(hfa)(COD) solution ink deposited on glass cured at 200°C for 10 minutes. Left: Ethanol solvent; Right: Toluene solvent.

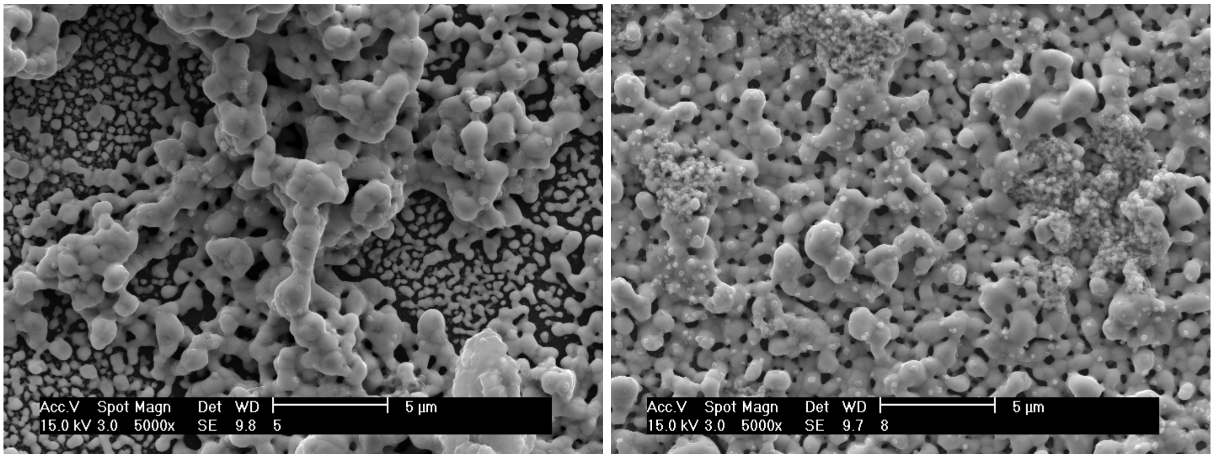

Figure 37: Solvent types affect the pattern of Ag(hfa)(COD) solution ink deposited on glass cured at 300°C for 10 minutes. Left: Ethanol solvent; Right: Toluene solvent.

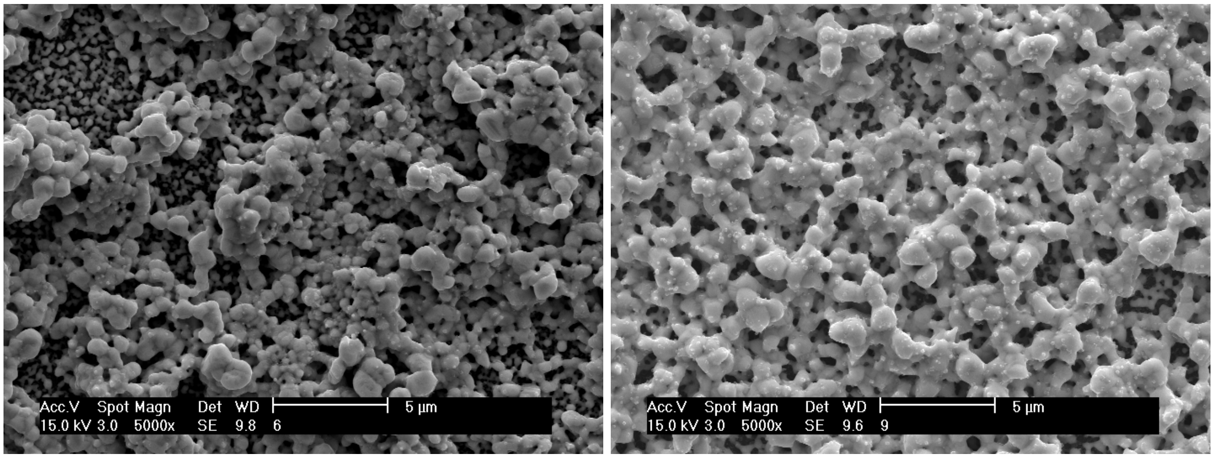

Figure 38: Solvent types affect the pattern of Ag(hfa)(COD) solution ink deposited on glass cured at 450°C for 10 minutes. Left: Ethanol solvent; Right: Toluene solvent.

To consolidate the solid structure and make a solid film, the above samples were further annealed in an oven at 580°C for 30 minutes. It is found that loosely porous particle clumps were consolidated to a continuous solid film. Porosity is significantly reduced from the observed shrinkage in the thickness direction. There are still small 'pores' in the film because there is not enough material to compensate for the material shrinkage. The thin deposition position in Figure 38 was reasonably supposed to become the source of pores in Figure 39.

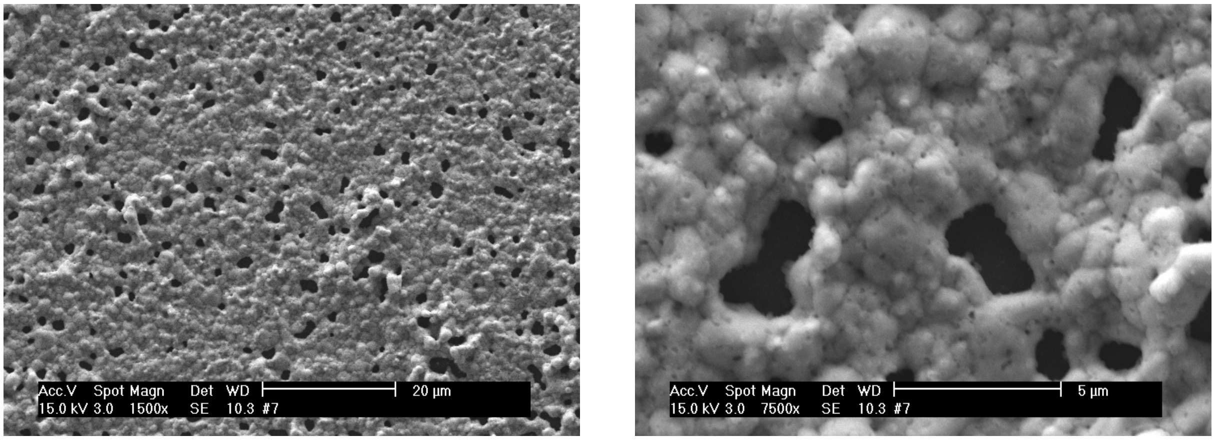

Figure 39: 0.5gram of COD dissolved in 1ml ethanol; consolidation from 580°C for 30mins.

The consolidated structure has electric resistivity lower than the more porous structure before consolidation, but the resistivity is still five times higher than that of bulk silver. The higher resistivities compared to bulk metal are probably not only due to impurities but also to the presence of pores in the silver film (Figure 39). The silver percentage of Ag(hfa)(COD) is only 25.6wt%, so Ag(hfa)(COD) is not an efficient precursor in depositing pure silver film because nearly 75% of the materials are evaporated in the gaseous phase and thus leave the system. The large variation in thickness of the deposited metal film is determined by the MOD precursor physical / chemical nature, curing temperature and the solvent as well; the selection of MOD precursors is the most critical determinant of the three factors indicated.

5.3 SILVER NEODECANOATE

An organic solution of metallo-organic silver compound of silver neodecanoate is investigated in this section. The molecular formulation is $C_{10}H_{19}AgO_2$. The selection of ten carbon atoms is a good compromise between solubility and metal content. Silver neodecanoate is very soluble in xylene, toluene, and benzene. Benzene could be an option, but it is more detrimental to people's breath system and should be avoided as the solution vehicle. The melting point of silver neodecanoate is 106~116^{o}C. It has been reported that silver neodecanoate begins to decompose at 175^{o}C, has its maximum decomposition rate at 230^{o}C and all carbon is gone at 250^{o}C [39,45,46]. By firing at a temperature of 300^{o}C, a uniform conductive line film was produced with titanium or palladium thin film underlayer as an adhesion promoter for the multilayer inkjet printing. There are two steps for synthesis silver neodecanoate:

Step I: Neodecanoic acid is converted to ammonium neodecanoate.

$C_9H_{19}COOH + NH_4OH \rightarrow C_9H_{19}COONH_4 + H_2O$

Step II: Ammonium neodecanoate is then converted to silver neodecanoate.

$C_9H_{19}COONH_4 + AgNO_3 \rightarrow C_9H_{19}COOAg + NH_4NO_3$

The two-step simple synthesis and abundant resources make silver neodecanoate commercially available with a much lower price than Ag(hfa)(COD).

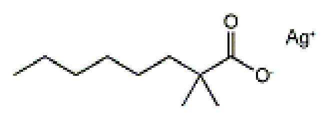

Figure 40: The molecular structure of silver neodecanoate.

This comparison of silver weight contribution in MOD compounds is very important because sufficient precursors should be put in a certain volume of conductive ink to make narrow conductive traces with good conductance. According to the metallo-organic decomposition method, all of the elements except the metal phase will decompose and recombine in a certain form of a gaseous phase and evaporate into environment. The molecular weight of silver neodecanoate is 279.12 with a silver contribution of 38.7%, while Ag(hfa)(COD) has an M.W. of 422 with a silver percentage of 25.6%. The less the metal silver in the compound, the more the gaseous phase will leave the solid phase producing higher porosity. From the previous discussion, we understand porosity is the big problem in printed structures. The electrical conductance and mechanical strength of a porous structure are far below the corresponding properties of dense metal.

Assume that 20wt% silver should be included in toluene for dense ink. For Ag(hfa)(COD), 2.61 gram of the compound needs to be dissolved in toluene. This specification is not possible for Ag(hfa)(COD) because it has solubility of only 0.6-0.7 gram in toluene at room temperatures;

While for silver neodecanoate, only 0.92 gram compound needs to be dissolved in 1 ml toluene to make 20 wt% silver solution, which is completely acceptable.

Considering the gaseous product from decomposition of these two compounds, silver neodecanoate has three elements besides silver, which are carbon, hydrogen and oxygen. The possible by-product gaseous phases are within the categories of carbon dioxide, water, etc, which will not cause detrimental effects to the user's health. Fluorine in the composition of Ag(hfa)(COD) will form a very erosive compound of HF and extra precautions must be taken. From the comparison, we can deduce that silver neodecanoate is a promising precursor to make conductive traces with low porosity, high conductance and strong mechanical strength.

As the experiments were designed, 0.92 gram of silver neodecanoate was dissolved into 1ml toluene to make 20wt% solution ink for the inkjet printing. The fluid properties were tested as:

Density: 1.16 gram/ml

Surface tension: 29.7 dynes/cm

Viscosity: 2.83 cps

These rheological properties are just within the optimum range of continuous inkjet printing (table 1). The solution was deposited on polyimide, and cured in a stove of $300^{o}C$. The color changed to dark. Instantly, brown fume formed which left the system, and finally, metallic silver formed on the substrate. The entire process can be completed in a few minutes. Elongation of the curing time does not help increase the electrical conductance. Hot plate curing at $250\sim300^{o}C$ is sufficient to decompose silver neodecanoate into metal phase to save processing time and energy.

The silver neodecanoate conductive ink was also deposited on a glass slide and the solvent evaporated. Silver neodecanoate melted at $110^{o}C$ and became a dark thick oily paste. The deposited trace was then cured in an oven of 300°C for 5 minutes. Looking at Figure 41, it is a densely packed 100nm particle aggregation. The metal silver is just evenly and uniformly covered through the surface of the substrate as expected. This intimate clinging to the substrate is preferred to maximally reduce the porosity and to increase the adhesion.

Table 7: Comparison between silver neodecanoate and Ag(hfa)(COD)

	Formula	Bond to silver	Silver contribution to W.M. %	M.P. °C	To reach 20wt%, weight to be dissolved in 1ml of toluene.
Silver neodecanoate	$C_{10}H_{19}AgO_2$	Ag-O	108/279= 39%	106~116	0.826
Ag(hfa)(COD)	$C_{13}H_{12}AgF_6O_2$	Ag-O	108/422= 26%	122~124	2.61

The section geometry was measured with a profilometer for calculation of the resistivity (Figure 42). For a silvery metal trace of 2.54 cm long, 2.0 mm wide, 0.8 μm thick, the electric resistance is 0.4 ohm. Thus the electric resistivity is 2.4~3.2E-8 ohm.m, only 1.6 to 2.0 times that of bulk silver. The metal trace was brittle and can be peeled off or rubbed away with a hard object. The electrostatic forces were not formed between the decomposed silver and glass substrate. Sealing with a top layer of epoxy may be the solution. A polymer binder in the ink composition may impede electrical conductivity and is not preferred.

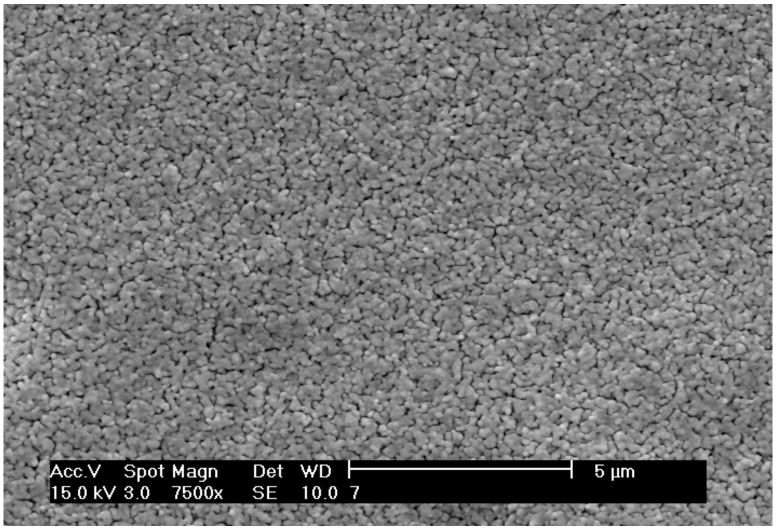

Figure 41: Dense structure of decomposition product of silver neodecanoate before high temperature annealing.

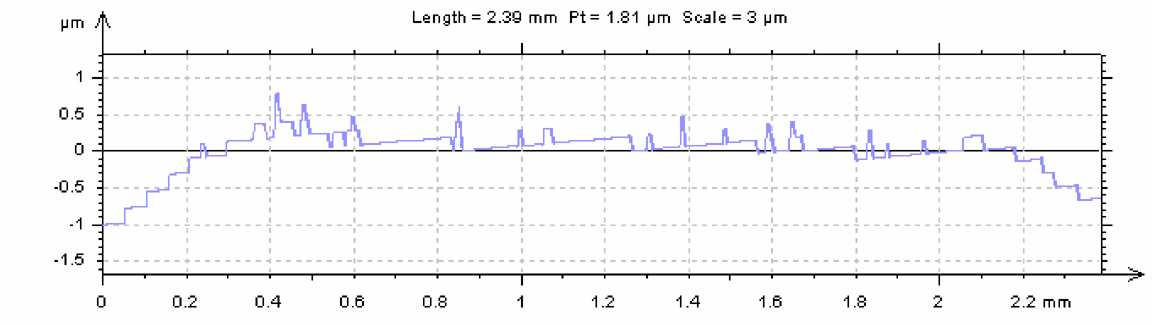

Figure 42: the geometry on the section of silver conductor deposited with silver neodecanoate solution ink.

It must be admitted that the dense silver film in Figure 41 is not a continuous solid silver film. The electric conductivity is not as good as that of bulk silver, and the mechanical strength is low. To increase the comprehensive properties, the silver trace was further annealed in an oven of 580°C for 30 minutes. The 580°C annealing temperature was chosen because higher temperatures, for example 700-900°C, are out of the range of glass transition temperature. The glass plate will deform significantly and deteriorate the quality if curing temperatures are higher than 600^oC. A temperature of about 575^oC for around 30 minutes has been proven to be effective in the following:

- Complete evaporation of residues;
- Consolidate the traces;
- Make silver penetrate into silicon oxide, giving a strong bonding between the metal film and the glass substrate.

The annealed product has the properties of bulk silver, including electric resistivity and mechanical wearing resistance. This temperature range of heating has been proven not to affect the properties of the general glass materials.

The metal particle aggregation were transformed into a high density solid metal film with a new crystal in size of 1~5 microns (Figure 43), about 10~50 times the increase in grain size during densification, with small residual pores located on grain boundaries (comparing with Figure 41). The film formed on glass is an intimate-packed, gapless solid crystal structure. Electrons can be directly transmitted through the film without significant hindrance. The electric resistivity is measured to be 2.0E-8 ohm.m, very close to electric resistivity for bulk silver (1.6E-8 ohm.m).

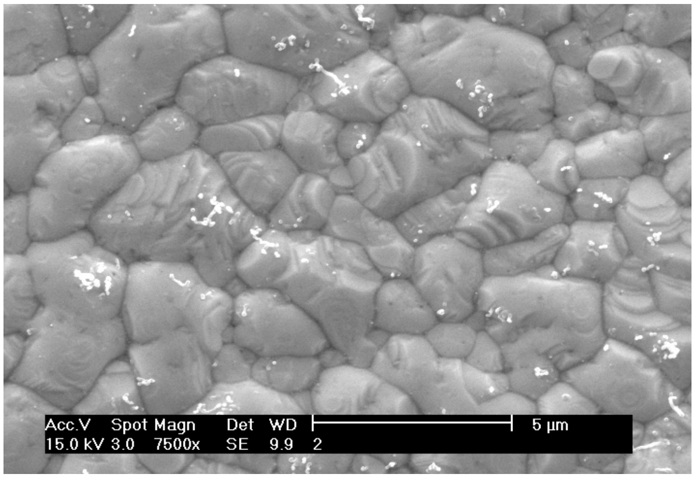

Figure 43: Consolidation of the structure above after high temperature annealing.

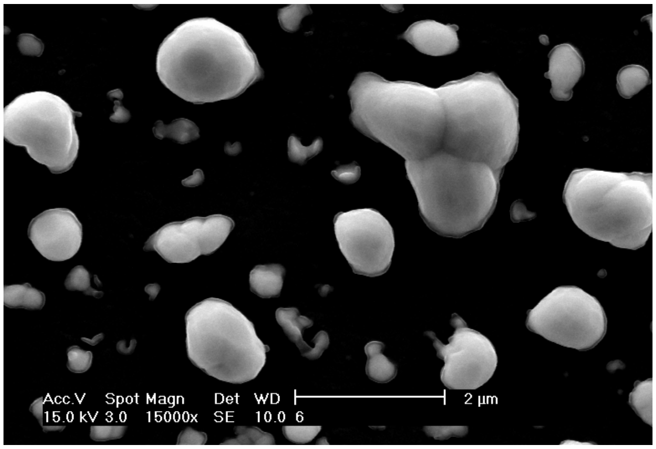

Figure 44: Separate consolidated particles when the conductive ink is not densely deposited; Conductive ink contents, and curing parameters are all the same as that of Figure 43.

The SEM micrograph of Figure 44 shows the case of separate crystals after high temperature annealing if the conductive ink is not densely deposited. Compact densification is accompanied by dimensional shrinkage with the disappearance of pores, and the particles grow in the consumption of nearby material if enough is available. When the compound is not densely deposited, there is not enough material to compensate for the consumption; and subsequently the big crystals were separated by vacant spaces. During this process, a few large grains show growth while small ones disappear.

The consolidated film shows the ductile deformation similar with bulk metal silver if scratched. The wear resistance of the final trace is greatly improved. A scratch test was carried out on pin-on-Disk Tribometer System. The parameters are set as:

Abrasion tool: ½ inch (Diameter) steel ball

Tip loading: 125g

Running circle radius: 15 mm

RPM: 75

For the one inch length with the steel ball sliding through, the electric resistance was remained at as 0.4 ohm even after 5000 cycles of abrasion.

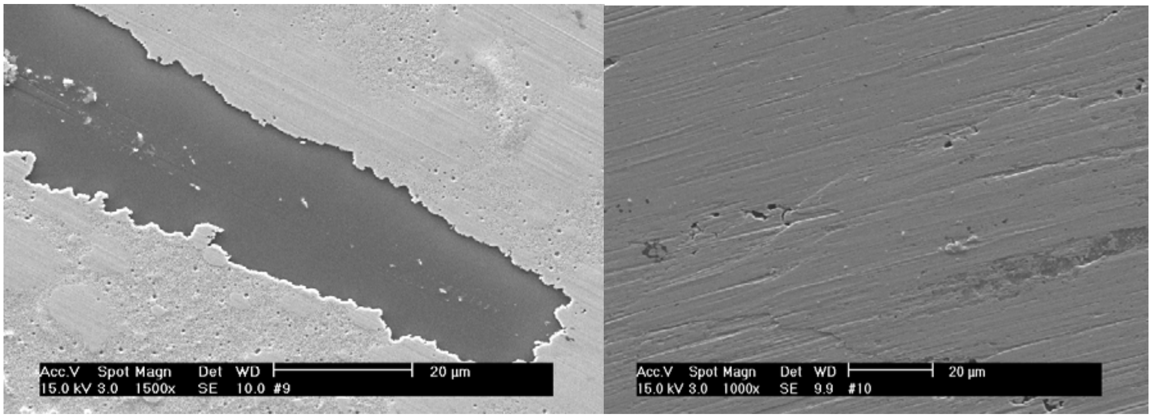

Figure 45: Left: Brittle feature during abrasion test with 125 gram loading after only 20 cycles; right: Ductile feature during abrasion test with 125 gram loading after 100 cycles

Figure 45 shows the different wear patterns for samples before consolidation and after consolidation. The wear test is on the same Pin-on-Disk tribometer with loading of 125gram on the ball tip. These two conductive traces are taken from the same printed trace line with the same conductive ink. The only difference is that the left side is only cured at 300°C for 5 minutes with a porous microstructure as shown in Figure 41, while the right side material has continuously cured at 580^{o}C for 30 minutes with consolidated microstructure in Figure 43. A typical brittle fracture pattern was observed after only 20 cycles of the wear test. The silver trace was completely cut through and lost its electrical conductance. The right photo, taken after 100 cycles of the wear test, was a typical ductile pattern against the hard ball scratch. The conductive material is still continuous and the conductance loss is negligible. Because metal silver is relatively soft compared with steel, the abrasion during test changes the original crystal profile; but through the ductile deformation, the metal strongly adheres to the substrate instead of being chipped off. The increase in the electrical conductance has been observed at the beginning period of wear test from the densification effects.

The trace profile does not depend on the surface property of glass, and thus it does not need specific cleaning. The color of the trace is silver and the opposite side of glass is golden thus aesthetically appealing for both decoration and electronic functional purposes.

5.4 DISCUSSIONS AND SUMMARY

Two different silver MOD compounds of silver neodecanoate and Ag(hfa)(COD) were researched for the purpose of optimizing the final properties. Evidently, silver neodecanoate was shown to have advantages over Ag(hfa)(COD) considering the comprehensive properties of electrical conductance and mechanical adherence.

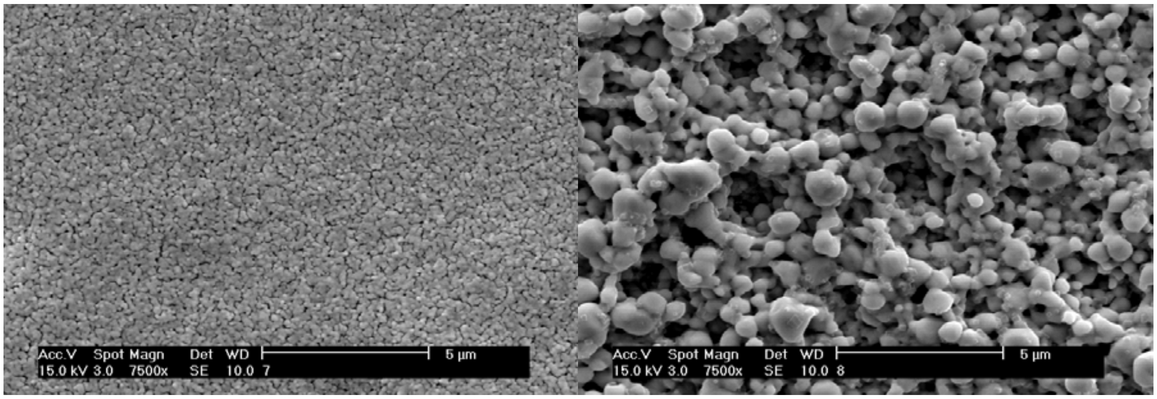

Figure 46: Compare the porosity between two printed conductors cured at 300^{o}C for 20 minutes. Left: Deposited with silver neodecanoate solution ink; right: deposited with Ag(hfa)(COD) solution ink.

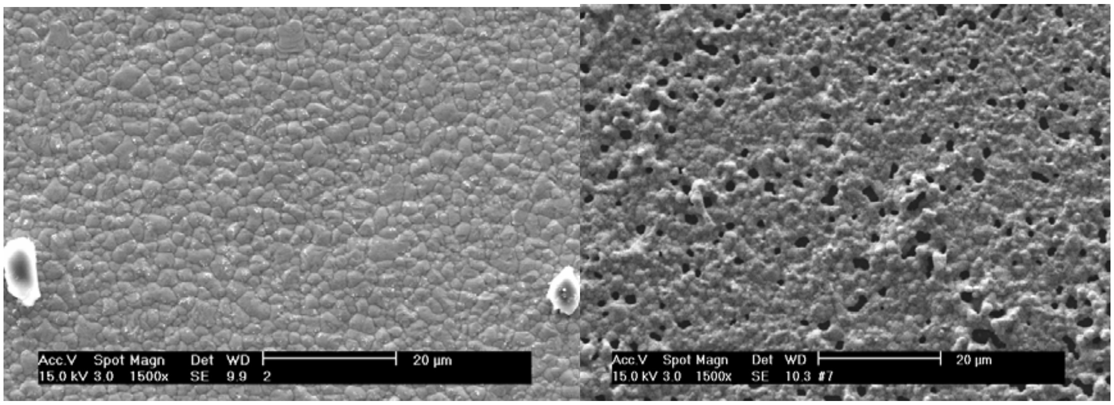

Figure 47: Compare the porosity between two printed conductors cured at 300^{o}C for 20 minutes and further annealed at 580^{o}C for 30 minutes. Left: Deposited with silver neodecanoate solution ink; right: deposited with Ag(hfa)(COD) solution ink.

The microstructures of two different MOD inks are placed side by side to show how the chemical nature of the precursor determines the properties of the conductive traces. The silver layer from curing the precursor of Ag(hfa)(COD) at 300^{o}C was a porous structure (Figure 46) and not as closely packed as the conductor printed with silver neodecanoate. With further annealing at 580^{o}C for 30 minutes, both the structure from silver neodecanoate and Ag(hfa)(COD) have been consolidated (Figure 47). For the silver neodecanoate deposited conductor, the further annealing produced a perfect continuous solid film without zero porosity. After consolidation, the electrical resistivity is close to that of bulk silver. The wearability is also improved from the ductile deformation. For Ag(hfa)(COD), the consolidated silver is still a porous film with many ‘caves’ distributed within. The electrical resistivity is several times that of bulk silver, and the traces can be scratched off easily.

Furthermore, sublimation was observed to accompany with the decomposition process of Ag(hfa)(COD). Material was found deposited during the curing process on the nearby substrate where the conductive ink was printed. It is not a good phenomenon because the sublimation during curing will spoil the geometry resolution. Sublimation did not happen to the silver neodecanoate during the entire process. The resolution was perfectly preserved as originally printed.

Based on above reasons, silver neodecanoate is an ideal precursor for conductive inks. It is a little more expensive than the aqueous silver nitrate solution ink. When the production is in small scale, the electrical conductivity is critical and very fine resolution is required, silver neodecanoate conductive ink is the best choice.

It also needs to be claimed that for temperature sensitive substrate, global curing in an oven should be avoided because the substrate is not able to stand the high temperature required to consolidate the conductive traces. In these cases, local heating methods such as a laser beam are considered to consolidate the porous metal pattern into solid films, and the substrate is protected from overheating.

6.0 DISCUSSION ON FORMULATION AND PROCESSING OF CONDUCTIVE INKS

6.1 SINTERING THEORY TO REDUCE POROSITY

Sintering is defined as a thermal treatment for bonding particles into a coherent, predominantly solid structure via mass transport events that often occur on the atomic scale. Bonding leads to improved strength and lower system energy. Pores are an inherent part of sintering. They are present in the powder compact as interparticle voids, forming a three-dimensional network. The consolidation densifies and reduces the pore size. Many properties such as strength, conductivity and fracture resistance undergo dramatic improvements during the consolidation of porous structures.

Sintering lowers the surface energy by reducing the surface area with concomitant formation of interparticle bonds. The bonds grow by various mechanisms that occur at the atomic level, such as solid state diffusion, solid-liquid phase sintering, etc. Melting is a phenomenon where the solid phase is transferred into liquid phase, which may be one of the mechanisms of sintering but far from being required. It is important to understand the difference between these two physical phenomenons. Comparing with sintering, melting needs a higher surface energy and depends on relatively higher temperatures to further activate the atoms. The melting points can be predicted for small particles based on the theory that the high surface area to volume ratio ensures the surface energy is high, which is the impulse for melting at relatively low temperatures. But it was found that nano particle conductive inks can form a continuous solid film at even lower temperature than predicted. For example, nano-gold particles can be sintered into continuous metal film at only 175^{o}C (Figure 8). It can be concluded melting is not be the only mechanism during curing of conductive inks. It is typical for particles to sinter bond together and consolidate to solid films.

There are various mechanisms for sintering of consolidation, such as

- Solid state diffusion, a process of atoms mass transportation in the solid state, which dominates the low temperature sintering far below the melting points;
- Solid-liquid phase sintering, where partially melting occur resulting solid-liquid mixture during the thermal cycles. Many sintering cycles generate a liquid. It may be present momentarily or may persist during much of the sintering cycles. The liquid phase provides bonding contributing a capillary force and enhancing the rate of mass transportation as compared to the solid state process. It also exerts a capillary pull on the particles that is equivalent to a large external pressure. Presence of a liquid in the cycle accelerates mass transfer, densification, and microstructure coarsening.
- Chemical reaction is involved between powders, producing more heat under the condition of an exothermic reaction. The chemical reaction could be the most important mechanism in particle-free solution inks. In both of the silver nitrate solution ink and the silver neodecanoate ink, a pure metal phase was produced through thermolysis reaction. The conductors deposited with these two inks were found to have strong adherence to the

glass substrate. It is believed the electrostatic bonds were created through chemical reaction with the substrate.

- For the irregular shaped particles, surface energy is not evenly distributed. It is possible that the melting is initiated at the tip of particle where surface energy is high, which can explain why the silver flakes of 10 microns in size can be cured at 300^{o}C and interconnected on the ends of flakes (Figure 20).

In sintering, two elements determine the mass transportation process, first is the internal surface energy, which directs the mass flow; second is the atom mobility, which is directly related to temperature. For higher temperatures, sintering is faster because of the increased number of active atoms and violable sites. The following factors affect the sintering:

- Temperature
- Particles size
- Pressure
- Liquid phase
- Sintering time
- Heating rate
- Process atmosphere.

The curing of printed conductive inks is a special application of general sintering. First, it is two dimensional sintering because the printed material is thin in the third direction and the constraints in the thickness direction are not significant. In practice for general sintering in a 3-D space, fast heating is avoided because of thermal shock which may damage the powder compact. Second, the curing of conductive inks is generally accompanied with chemical reactions. Gaseous phases may be produced as well as extra heat. From this point of view, curing conductive traces is more complex phenomenon than pure metal particle sintering, considering the distribution of temperature, heating rate, and process atmosphere, etc. Further reduction in the sintering temperature can be achieved by chemical additives for an exothermic reaction.

Further research should be carried out based on the theory of sintering if we admit the curing conductive inks is essentially a sintering process. The research results can be used directly to guide the formulation and processing of conductive inks for better properties.

6.2 ADHERENCE PROMOTER

Adhesion is defined as the binding force exerted by molecules of unlike substances when brought in contact [47]. The strongest molecular level bond is the shared electron bond. The bond is based on forces that develop when atoms share orbital electrons. For the shared electron bond to become effective, the atoms must come so close to each other that their electron shells penetrate. Metal and metal alloys form shared electron bonds between atoms.

Electrostatic bonding is responsible for a different kind of adhesion mechanism. This bond is based on electrostatic forces between molecules having electrical poles. The molecules, when in close contact, will try to orient themselves so that the poles of opposite polarity hold on to each other. Shared electron bonding can be obtained at relatively low temperatures as long as the atoms come close enough to allow their orbits to merge.

A weak form of electrostatic bonding is caused by a shift of the electron orbits in an atom. The centers of the positive and negative charges do not always coincide. Oscillation for the charge centers results in a dipole moment that causes electrostatic forces, called Van der Wall forces, between atoms. These bonds, although weak, will assist in bonding when stronger molecular bonds are not established.

Oxides are usually electrically polarized because an exchange of electrons between an element and the oxygen atom is the basis of the molecule formation. The electron load is not centered in the oxide molecule. Ionic bonds are stronger than dipole bonds and result from a chemical reaction. Electrons are exchanged across the adhesive bond line, creating a strong electrostatic field between the materials. Metal oxide and glasses are bonded by electrostatic forces.

Adhesion and chemical reaction are closely related and are sometimes the same. A condition for good adhesion is the chemical compatibility of surfaces to be bonded. In the current investigations, a solid bonding is required to setup between noble metal films and glass substrate. Gold or silver will form only shared-electron bonds and has no affinity for oxygen. Glasses form electrostatic bonds and contain oxygen as an essential component. A direct molecular bond of gold or silver to glass is impossible because the bonding mechanisms of the two materials are incompatible. The problem is overcome in thin-film technology by the vacuum deposition of intermediate materials on the glass before the gold is deposited.

To form a molecular bond between precious metals, such as silver or gold, and ceramic materials require a metal and metal-oxide link. To form such a link, metal-oxide additives must partially be reduced to metals to form an alloy type shared electron bond with the precious metal. Oxide reduction occurs at the firing temperature at which maximum adhesion results. It can be assumed that the liquid metal oxide penetrate the substrate structure and on cooling forms oxide crystals held to the ceramic with an electrostatic bonding.

In the aqueous silver nitrate conductive ink, the conductor formed by the decomposition of only silver nitrate is found to be weakly bonded with glass substrate. To increase the adherence, aluminum nitrate nonahydrate was added in the formulation as an adhesion promoter, which decomposes into aluminum oxide around 500°C as the interface to bond silver and glass substrate. To form a molecular bond between silver and glass requires a metal and metal-oxide link. The oxide addictives must be partially reduced to metals, which is possible at high temperatures. When the oxides are exposed to temperatures close to their melting and decomposition point they lower their oxidation state, become metallic during the transition, and form an alloy type shared electron bond with precious metal. It can be assumed that the liquid metal oxide crystals held to the ceramic with an electrostatic bond possibly based on a chemical reaction.

For the MOD conductive inks, metallo-organic materials contain small amounts of base metal oxide (or glass forming metal resinate) to provide adhesion of the metal film to the substrate. When the ink is fired, these base metal oxides or glasses interact with both the metal and the substrate wetting both and producing a strong bond. Because MOD films are thin, stresses caused by thermal expansion mismatch are minimized, resulting in excellent adhesion. Adhesion to metals requires a clean metal surface similar to the requirements for soldering. Acid constituents in the MOD act as fluxes to promote adhesion.

6.3 LASER CURING, GAS JETTING, AND FUTURE WORK

As discussed in previous chapters, good comprehensive properties are achieved through curing and consolidation, which is generally a high temperature stove heating process. The required high temperature curing places great limitations on the application of conductive inks with temperature sensitive substrates such as poxy-fiberglass, phenolic fiber, or polyimide. The techniques to further reduce the curing temperature are not practical and may cause other side effects. For example, nano-gold particles and some gold MOD compounds can be cured at 150°C for conductive films, while the expense itself places anther limitation.

By "thinking outside of the box," it is possible to achieve the same consolidated properties through other energy resources so that the substrate is minimally affected. Laser curing is one of these methods that are effective to break through the limitation of stove curing methods and attract more research interests in this area.

Laser curing enables local heating, so that thermally sensitive circuits in other areas can be protected. In addition, the laser energy is directly absorbed by the printed line on the substrate, so that the thermally affected zone on the substrate can be minimized. Using a modified drop-on-demand jetting system, the gold nanoparticle colloid is printed on a glass substrate and cured with laser irradiation [48]. The laser energy in conjunction with thermocapillary effects and the evaporation of the solvent are critical to the quality of the electrically conductive gold microlines. By employing an intensity –modulated double laser beam processing scheme to optimize the curing process, it is demonstrated that for the first time that the gold nanoparticles can be sintered on a glass substrate to form a gold line of resistivity close to that of bulk gold. However, as mentioned previously, nano-gold is costly for many general purpose applications. But if the laser technology is coupled with the two silver solution inks introduced in previous chapters to achieve the bulk silver properties, the cost will be significantly reduced.

For laser curing, the selection of wavelength is the most critical part of the technology, which determines what percentage of energy will be absorbed by the conductive ink and by the substrate respectively. High absorption by the substrate will deteriorate the advantages of local heating for laser curing and even melt the substrate. The wavelength can be selected by a study of the dependence of the absorption depth of the suspension on the wavelength of the incoming laser radiation so that most of this radiation is absorbed in the close vicinity of the printed lines [49]. Another method is to test the absorption spectroscopy curve over various wavelengths for a specified precursor, for example, silver neodecanoate. Then pick the peak wavelength of maximum absorption and make sure this wavelength does not heat on the substrate.

A gas jet is another category of 'jet printing' process to deposit the micro-scale particles on glass, metal, or plastic substrate without inclusion of any thermal resources. Actually this technology has been reported in 1986 by Kashu to deposit ultra fine particles (UFP) of Ag, Fe, Ni, Cu, Au, Ti, Pb, Zn, TiN and RuO_2 [50]. The particles were entrained in a gas flow in a tube and accelerated. With a sufficiently high velocity (bigger than 100 m/s) of jet flow against the substrate, the UFP will have sufficient energy released at the collision to stick to the substrate and to each other successively. With a tiny nozzle, 0.3mm in diameter, a line pattern 0.3mm wide can be deposited. For the deposit, a green density of over 55%, which corresponds to a high pressure press, is obtainable. Flotation and transportation of two or more different kinds of particles for the deposition from a single nozzle is possible regardless of the specific density of each kind of particles.

A similar flow guided deposition is introduced by the research group at Superior MicroPowders LLC [51]. An aerosol stream passes through an initial orifice serving as the primary focusing point. The purpose of the sheath gas is to form a boundary layer that both focuses the particles stream and prevents the particles from depositing onto the orifice nozzle walls (Figure 48). This shielding effect minimizes clogging of the orifices and reduces contamination during transitions to a different material. The emergent particle stream, which is now wrapped in the sheath gas, is focused to approximately 20% of the diameter of the second orifice. The beam diameter, and consequently the line width on the substrate, is controlled primarily through the sheath gas flow rate. Increasing the sheath gas flow rate will tighten the deposition beam and create narrower deposition lines. Different from the gas jetting, this technology is essentially an inkjet printing method. The material hitting on substrate is in fluid state and subsequently oven curing is required. The sheath gas was used for further reduction of the minimum feature size.

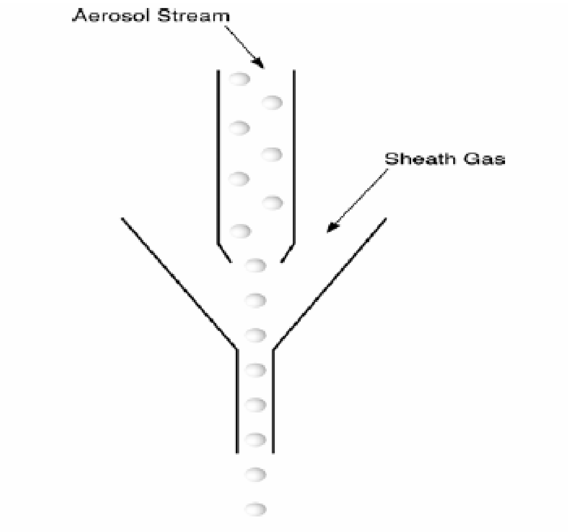

Figure 48: Concept drawing of flow guide head, showing the particle stream, focusing orifice, and the sheath gas flow.

A nano-particle pattern is reported to be self assembled onto charged surface areas with a resolution of 100~200 nm [52]. By applying a voltage pulse between the conductive electrode and the silicon substrate, the charged pattern was transferred into the thin film to attract nanoparticles. Areas as large as 1 cm square were patterned with charge with 100nm scale resolution in 10s. Nanoparticles were generated using a tube furnace by evaporation and condensation at the outlet. The electrostatic directed assembly of 10-100nm sized metal and 30 nm sized carbon particles was accomplished with a resolution 500-1000 times greater than the resolution of existing xerographic printers.

The advantages of gas jetting electric components concentrate on the flexibility of deposition materials and the substrates. There is no strict limitation of the categories of particles that can be gas jetted; even two different particles can be gas jetted through a single orifice. Since there is no post-curing required for consolidating the deposited material, it is applicable to deposit on plastics that are temperature sensitive. However, it has been found that even though in gas jetting large particles (size over 1 micron) tend to maintain a straight-line trajectory from the nozzle to impact on the substrate; smaller particles (nano-scale) predominately follow the gas stream shear flow, which is tangent to the substrate.

Based on the paper review, a novel direct patterning of nanoscale particles on nearly any substrate is proposed. The proposal uses some conception of gas jetting, for which no post curing is required. The idea is that certain amount of nanoparticles can be put in one droplet of continuous inkjet printing through formulation of the nano colloid and modulation of the CIJ system. The solvent can be completely evaporated and the dry nano coagulators can be charged. An electrostatic field can be used to focus and accelerate the particles at speeds up to 100 meters per second. Similar to gas jetting, the particles can impact on the substrate, and release sufficient energy at the collision to stick to the substrate. With this direct-write technology, electronic components can be patterned with high density and very fine resolution.

7.0 APPLICATIONS

The investigators have constructed a specialized continuous inkjet 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 49, the constructed print head includes all of the standard mechanical components required for continuous inkjet 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 50. 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 51, is computer programmable and has an accuracy of 100 nanometers.

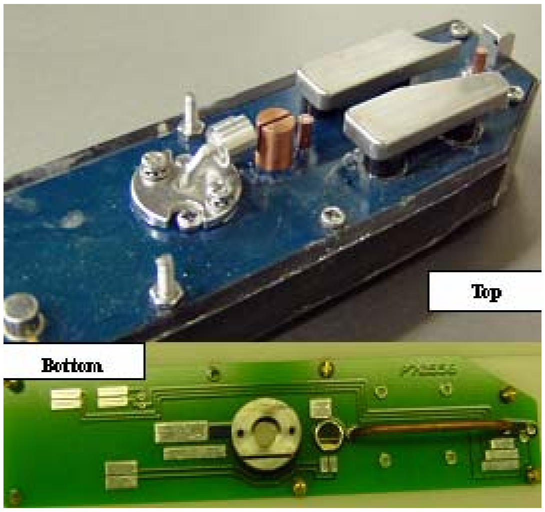

Figure 49: CIJ printing head.

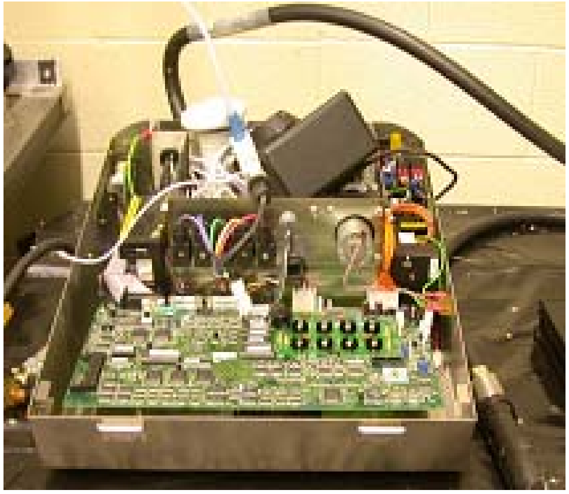

Figure 50: CIJ printing control system.

Figure 51: Motion table.

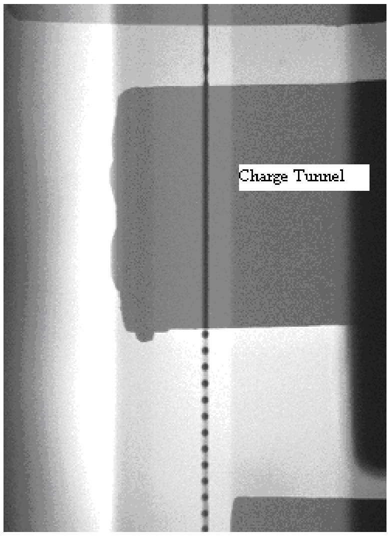

Figure 52: Stable droplets generated and charged from CIJ system.

Once the aqueous conductive ink was generated, the continuous inkjet 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 52) by adjusting the fluid pressure, the voltage and frequency of the PZT crystal, and the charge tunnel pulse. The drop rate can be adjusted through the control of the percentage of the droplets being charged. For the aqueous solution based on silver nitrate, the pressure was set to be 10.5 psi and PZT frequency was set to be 26 kHz to get droplets with uniform size and stable gaps between sequential drops. There are 125 droplets being charged and injected through the deflection plate, while those left uncharged were collected and re-circulated through the gutter. Droplet diameters produced were in the range of 100μm and the droplet velocity was approximately 4m/s. This aqueous silver nitrate solution ink was found to possess good viscosity and surface tension properties; so it was able to produce conductive traces (Figure 53) similar to windshield heating grids after heating at 485^{o}C for 20 minutes. The resolution of the grid lines was 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.

To demonstrate the ability of the CIJ system to print in three-dimensional space, 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^{o} angle to the axis of the inkjet head, as indicated by the dashed lines in Figure 54(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 54b). Two very important characteristics of the printed system are demonstrated in traces shown in Figure 54b. 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 ^{o} to 45^{o}, which demonstrates that the CIJ technique is capable of printing on complex 3-D surfaces.

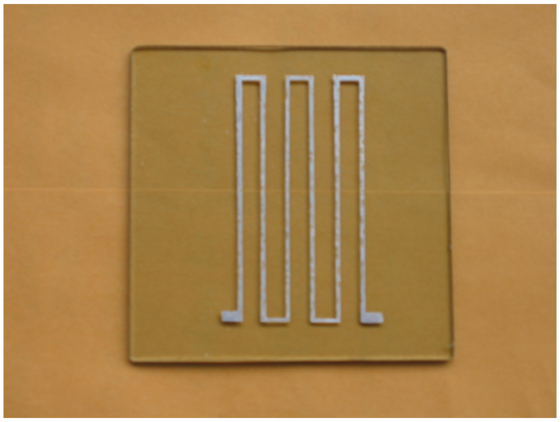

Figure 53: Sample silver heating grid.

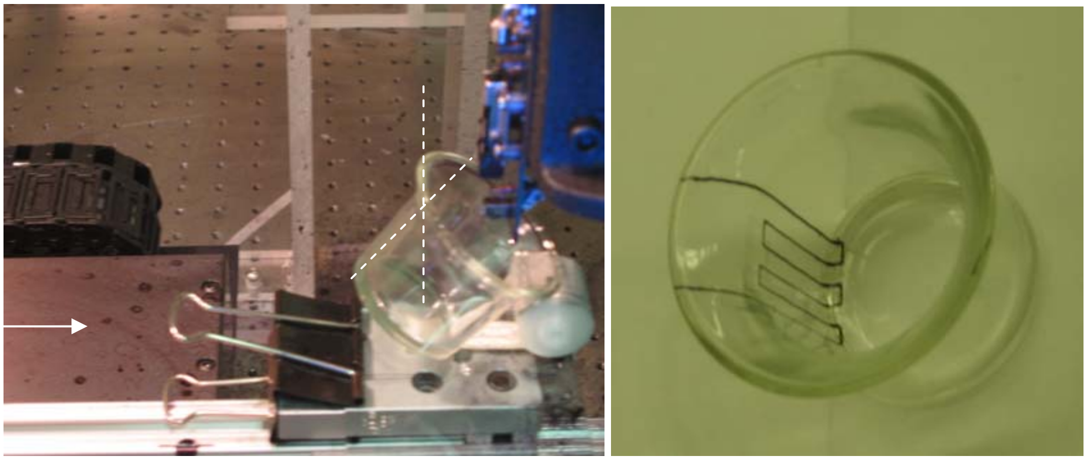

Figure 54: (a) The cup was fixed on the 2-D motion table; (b) Antenna pattern was printed on the 3-D inner surface of bugle cup with CIJ printing.

8.0 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 them, 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. The most important ingredient in the aqueous ink is a 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. 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.
2. A MOD silver compound was produced to be a precursor for a conductive ink that exhibited a dense microstructure. After consolidation, the MOD compound had a close-packed structure similar to bulk silver and exhibited excellent adherence. The electrical

conductance of traces produced was optimized to a resistivity value between 1 – 1.2 of that of bulk silver.

3. An in-depth discussion was focused on the topics of the formulation of conductive inks, the adhesion promoters, and consolidation of porous structures, which helps continuous optimization of conductive inks and the post processing procedures. An interlayer film was proven necessary for strong bonding between deposited precious conductive metal films and oxide substrates. Base metal organic or inorganic salts can work as adhesion promoters based on this mechanism. Porosity or separated metal particles is the general substructure for inkjet printed conductors. Consolidation is critical to transfer the loosely connected particles into a close-packed continuous solid film, which was endowed with excellent comprehensive properties. Laser curing or ‘gas jetting’ was proposed to consolidate the deposited conductors to avoid unnecessary heating the temperature sensitive substrates.
4. A 3-D capability with CIJ technology was demonstrated with printing antenna patterns the on the inner surface of a bugle-shaped cup. It is believed that further refining the CIJ process and ink material will allow the process to be used in the electronics fabrication industry.

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