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13. ABSTRACT (Maximum 200 words)

Flexible printed circuits have a wide range of applications in consumer electronics, computers, automobiles, and space and aerospace vehicles. In this Small Business Technology Transfer (STTR) Phase I program, Materials Research Institute (MRI) and University of Dayton Research Institute (UDRI) demonstrated the feasibility of a new processing scheme leading toward the fabrication of high-performance, low-cost flexible circuits with computer-aid design tools using the inkjet printing technology. Silver metal precursor solutions were studied for their viscosity and printability. Printed conductor patterns were evaluated on three commercially available polymer substrate materials. Research emphasis was focused on improving adhesion between the reduced conductor metal and the polymer substrate. Ag conductor patterns obtained from this processing scheme exhibited excellent electrical conductivity, mechanical integrity, and adhesion. This processing scheme is simple yet versatile. It can be readily extended to build multiple-layer circuits as well as circuits on a contour surface.

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Executive Summary

Flexible circuitry is a patterned array of conductors supported by a flexible dielectric film. It offers advantages such as flexibility, 3-D design capability, size and weight reductions, and high-temperature performance over the rigid printed circuit boards for a wide range of electronic devices in consumer electronics, computers, automobiles, and space and aerospace vehicles. As electronic and telecommunication devices become denser and more compact, flexible circuits find wider demand in both military and commercial applications.

Two basic techniques are currently used for the fabrication of flexible circuits. In the subtractive method, the unwanted portion of the copper foil on the flexible substrate is etched away, leaving the desired conductor pattern in place. In the additive method, formation of the conductor pattern is accomplished by adding conductors to a bare substrate in the pattern and other desired places. This can be done by plating copper, screening conductive paste, or laying down insulated wire onto the substrate on the predetermined conductor paths.

The conductor metals used for flexible circuits are usually electrodeposited or rolled and annealed copper foils, which are glued with adhesive on a polyimide or polyester base substrate. Flexible circuits are designed to allow 360° bending. Therefore, they have the advantages over rigid board circuits in lightweight and space saving. However, flexible circuits also have limitations due to their lightweight construction. For example, they are not designed for conducting high currents and need support to accommodate heavy chips and modules. They also may need support during fabrication procedures. As a result, flexible circuits have a higher manufacturing cost and are difficult to repair.

In this Small Business Technology Transfer (STTR) Phase I program, Materials Research Institute (MRI) and University of Dayton Research Institute (UDRI) investigated a new processing scheme leading toward the fabrication of high-performance, low-cost flexible printed circuits with computer-aid design tools and the inkjet printing technology. This processing scheme comprises three basic steps: (1) application of a metal precursor solution to form the pattern of a desired circuit on a polymer substrate, (2) evaporation of the solvent of the metal precursor from the substrate, and (3) thermal decomposition of the metal precursor to form the conductive circuit.

In this research, precursor solutions of silver nitrate in different organic solvents were evaluated for their wetting ability on three commercial polymer films currently used in the flexible circuits manufacturing. Solutions containing 40 to 50 wt% $AgNO_3$ exhibited good pattern forming ability on two of the polyimide films, Kapton® and Upilex®. The viscosity of these solutions (5 ~ 7 cP) was well within the proper range for inkjet printing applications. Ag conductor patterns on polyimide substrates with excellent conductivity were produced by heat treatment of the printed precursor patterns to 300°C in air.

Two approaches were investigated for improving adhesion and mechanical integrity of the Ag conductor on polyimide films. The first involved the modification of polymer substrates with a polyamic acid (PAA) coating and the second involved the addition of a polyamic acid binder in the precursor solution. Combination of these two approaches generated Ag conductor patterns exhibiting excellent electrical conductivity and good mechanical durability in both adhesive tape and folding tests. The resistivity of the Ag conductor was in the range of 10^{-4} to 10^{-5} Ω-cm, and was at the same level as that of the state-of-the-art polymer thick film technology.

These results successfully demonstrated that this processing scheme is feasible for fabricating next-generation flexible printed circuits using the inkjet printing method. This novel processing scheme takes full advantage of the current computer-aid design and manufacturing technologies, and has potential to be extended for fabricating multiple-layer circuits as well as complex circuits on a contour surface. In addition, this process is material saving and environmentally benign. A wide-range of lightweight, high-performance flexible circuits can be prepared for applications in consumer electronics, telecommunication devices, automobiles and space and aerospace vehicles.

1. Introduction

Flexible circuitry is a patterned array of conductors supported by a flexible dielectric film. It offers advantages such as flexibility, 3-D design capability, size and weight reductions, and high-temperature performance over the rigid printed circuit boards for a wide range of electronic devices in consumer electronics, computers, automobiles, and space and aerospace vehicles [1]. As electronic and telecommunication devices become denser and more compact, flexible circuits find wider demand in both military and commercial applications.

Two basic techniques are currently used for fabricating flexible circuits. In the subtractive method, the unwanted portion of the copper foil on the flexible substrate is etched away, leaving the desired conductor pattern in place. In the additive method, the formation of conductor patterns is accomplished by adding conductors to a bare substrate in the pattern and other desired places. This can be done by plating copper, screening conductive paste or laying down insulated wire onto the substrate on the predetermined conductor paths.

The conductor metals used for flexible circuits are usually electrodeposited or rolled and annealed copper foils, which are glued with adhesive on a polyimide or polyester base substrate. Flexible circuits are designed to allow 360° bending. Therefore, they have the advantages over rigid board circuits in lightweight and space saving. However, flexible circuits also have limitations due to their lightweight construction. For example, they are not designed for conducting high currents and need support to accommodate heavy chips and modules. They also may need support during fabrication procedures. As a result, flexible circuits have a higher manufacturing cost and are difficult to repair.

In this Small Business Technology Transfer (STTR) program, Materials Research Institute (MRI) and University of Dayton Research Institute (UDRI) investigated a new processing scheme leading toward the fabrication of high-performance, low-cost flexible printed circuits. In this processing scheme the circuits are designed by computer software packages such as CAD, CAM and other graphic routines. They are patterned on a flexible polymer substrate by inkjet printing with ink that contains a metal precursor, such as silver nitrate or acetate. After the ink is dried, the metal salt is reduced by thermal, chemical or electrochemical method to form a highly conductive circuit. In this Phase I program, research effort was focused on thermal reduction of the metal precursor due to its simplicity. Once the pattern of a circuit is printed, it is placed in an oven to remove the solvent and reduce the metal salt by heat.

This processing scheme is the simplest and yet the most versatile known method for preparing printed circuits. It takes full advantage of modern computer technology in both software and hardware. With the aid of a 3D computer graphic tool, it will allow complex circuits to be printed on a contour surface. Such a task is impossible to achieve with the current flexible printed circuitry techniques, which require masking and rolling copper foils onto the polymer substrate. The proposed technique can be readily extended to build multiple-layer circuits when a second cartridge is used to print an insulator layer over the conductor metal. In addition, it is also a material-saving and environmentally benign process. It prints only the conductive circuit on the polymer substrate and does

not require masking or striping of the photoresist. As a result, it uses less material and generates less waste. This processing scheme does not require large capital investment in machinery to produce flexible printed circuits. The high-performance, low-cost printed circuits are likely to find applications in space and aerospace vehicles and automobiles.

2. Phase I Technical Objectives

The goal of this STTR Phase I research is to demonstrate the feasibility of a processing scheme for fabricating flexible printed circuits by inkjet printing method. This processing scheme comprises three basic steps: (1) application of a metal precursor solution to form the pattern of a desired circuit on a polymer substrate, (2) evaporation of the solvent of the metal precursor from the substrate, and (3) thermal decomposition of the metal precursor to form the conductive circuit. Since the conductor metal is patterned on a polymer substrate from a solution, its wetting ability to the polymer is critical to the formation of a desired pattern. Equally important is the adhesion of the reduced metal to the polymer substrate, which will dictate the performance of the flexible circuit. Another critical factor for the success of this research is the viscosity of the metal precursor solution. It should be suitable for inkjet printing application. Our approach to processing flexible printed circuits by inkjet printing is through a fundamental understanding of the solution characteristics of the metal precursor and its interaction with the polymer substrate, leading to the formation of a conductive circuit that is thermally and mechanically durable.

The essential technical issues to be addressed in Phase I program are:

1. Solubility and solution viscosity of the choice metal precursor in organic solvents and wetting ability of the solutions to the selected polymer substrate.
2. Pattern formation of the metal precursor solutions and their reduction to form a highly conductive metal circuit.
3. Conductivity of the printed circuits and its stability under mechanical deformation and in thermal and mechanical cycles.

Our research is directed toward answering the following critical questions:

1. How to prepare the metal precursor solution suitable for inkjet printing and enhance its interaction with the polymer substrate to facilitate pattern formation?
2. How to maintain the pattern of a printed circuit throughout the entire printing, drying and reduction processes.
3. How to ensure the mechanical and thermal durability of the printed circuit for applications in space and aerospace vehicles and automobiles, where vibration is a primary concern.

3. Experimental Procedures

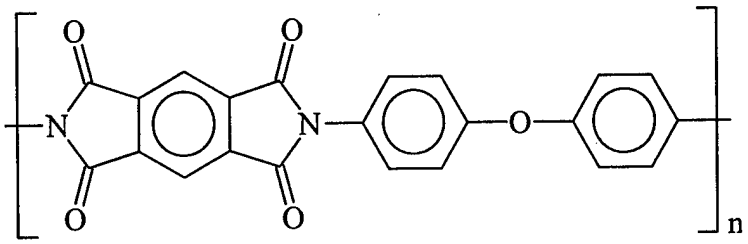
3.1 Materials

a. Polymer substrate

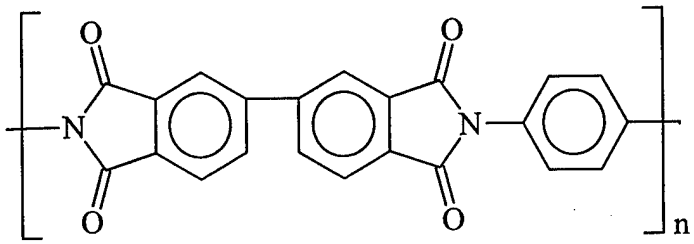
In this Phase I program, two commercially available polyimide films, Kapton® from DuPont and Upilex® from Ube, and one polyethylene naphthalate film, Kaladex® from ICI, were selected for the flexible polymer substrate. The chemical structures of these three polymers are illustrated in Figure 1. The selection of these three polymers was based on their thermal stability, chemical resistance and mechanical strength. In fact, these polymers have already been used in flexible printed circuits prepared by conventional technique. The precursors of the two polyimides, i.e., their polyamic acids, are soluble in solvents such as N-methyl-2-pyrrolidinone (NMP), dimethyl sulfoxide (DMSO) and dimthyl acetamide (DMAc). However, once the polymers are fully imidized, they show only a low degree of swelling in these solvents even at elevated temperatures. Therefore, the wettability of the metal precursor solution to the polyimides is an important factor to the success of the proposed processing scheme. Since only fully imidized polymer films are currently available, a layer of polyamic acid was coated on the polyimide films as one of the strategies to improve its interaction with the metal precursor solutions. In this case, the metal precursor solutions are likely to swell or partially dissolve the polyamic acid coating on the polymer substrate, resulting in infiltration of the metal precursor into the polyamic acid coating and leading to the formation of conductor metal, after reduction, partially embedded in the polymer matrix.

b. Metal precursor and its solution

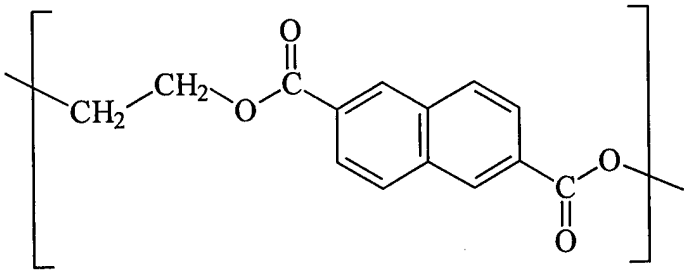
Silver is considered to be one of the best candidates for the conductor metal of printed circuits (see comparison in Table 1). It has excellent electrical and mechanical properties and is relatively inexpensive for fabricating printed circuits. Several silver salts, such as silver nitrate, silver carbonate and silver acetate, can be thermally decomposed into silver metal at moderately high temperatures. However, silver nitrate may be the best candidate for forming dense silver metal by thermal reduction, because it melts at 212°C before it decomposes into silver metal. This will guarantee a continuous phase of silver metal on the polymer substrate after thermal reduction and afford the conductivity of the printed circuit. Silver nitrate is soluble in water, NMP, DMSO and DMAc to a concentration up to 70 wt% at room temperature. In this Phase I research, silver nitrate solutions with concentrations up to 50 wt% were evaluated for their viscosity, their wettability to the selected polymer substrates, and the electrical conductivity of the conductor patterns derived from these solutions.



Kapton®



Upilex®



Kaladex®

Figure 1. Chemical structure of (a) Kapton®, (b) Upilex®, and (c) Kaladex®.

Table 1. Comparison of Metals Used for Flexible Printed Wiring Conductors [Ref. 2].

Conductor	Electrical Properties	Thermal Properties	Mechanical Properties	Relative Cost
Aluminum	Excellent	Fair	Good	Best
Copper	Excellent	Excellent	Good	Fair/Good
Gold	Good	Fair	Good	Excellent
Nickel	Good	Very good	Very good	Good
Silver	Excellent	Fair	Excellent	Excellent

3.2 Processing Scheme

Polymer substrates were cut into coupons approximately 2 in. long and 1 in. wide. The coupons were cleaned in a cleaning solution, dried, and stored in a container in DMAc. The basic processing scheme includes the following steps: (1) printing a precursor solution on a polymer substrate by either the doctor-blading technique or with a drawing pen, (2) drying in a vacuum oven or on a hot plate to remove the solvent at elevated temperatures, and (3) thermal reduction of the precursor patterns in a crucible furnace in air or under vacuum in a retort. During the heat treatment, the temperature of the furnace was raised slowly to melt and then to decompose the silver nitrate. In the doctor-blading technique, a spacer of known thickness was used to control the thickness of the solution layer, which determines the amount of silver to be coated on the polymer surface.

It is known that the adhesion between a passive metal, such as silver, and an organic polymer is weak. Two approaches were investigated to overcome this problem. The first approach involved modification of the polymer substrates with a thin coating of a polyamic acid (poly[N',N'-(1,4-phenylene)-3,3',4,4'-benzophenonetetracarboxylic imide/amic acid], Aldrich Chemical Co.). This polyamic acid (PAA) is soluble in organic solvents and therefore, may be swelled or partially dissolved by the silver nitrate solution during inkjet printing, resulting in the infiltration of the silver precursor into the polyamic acid coating. As a result, the subsequent reduction of silver nitrate will take place in the polyamic acid matrix. In addition, polyamic acid is a precursor for polyimide polymers. It is likely that the polyamic acid would imidize during the heat-treatment process and form good bonding with the polyimide substrate.

The second approach involved modification of silver precursor solutions by dissolving a modest amount of polyamic acid in the solution. When such a solution is being dried and its silver nitrate being melted and decomposed, all these events occur in a polymer matrix. Eventually, the polymer serves as an adhesive to glue the reduced silver and the polymer substrate together. Furthermore, the addition of the polyamic acid in the

precursor solution would enhance the dimensional stability of the printed circuits during printing and the subsequent thermal treatment. In the thermal reduction process, silver nitrate in the printed patterns would melt and thermally decompose in the matrix of the polyamic acid, which would be undergoing the imidization process.

3.3 Properties Characterization

a. Precursor Solutions

The wettability of a precursor solution on the surface of the polymer substrate is important for the solution to form, as well as to maintain a quality pattern on the substrate, and therefore is critical to the fabrication of flexible circuits by inkjet printing method. The contact angle between a liquid droplet and a solid substrate characterizes the wettability of the liquid to the solid. As shown in Figure 2, when a liquid drop is in contact with an ideally smooth, homogeneous solid, it exhibits an equilibrium contact angle, θ, which can be expressed by the Young's equation [3]:

$$\gamma_l \cos\theta = \gamma_s - \gamma_{sl} \qquad (1)$$

where γ_l is the surface tension of the liquid in equilibrium with its own vapor, γ_{sl} the interfacial tension between liquid and solid, γ_s the surface tension of the solid. A smaller contact angle indicates a better wettability of the liquid to the solid. A Tantec contact angle meter was used to measure the contact angles of various solvents and silver nitrate solutions on different polymer substrates. All contact angle measurements were made with a liquid volume of 5 μL. Some polymer substrates had been bathed in Windex® brand window cleaner or a concentrated HCl solution for five minutes prior to the contact angle measurement to investigate the effects of these surface treatments. The viscosity of silver nitrate precursor solutions was determined using a Cannon 75 Ubbelohode Viscometer with a constant temperature bath. The viscometer was calibrated against distilled water and the measurements were performed at a constant temperature of 30°C.

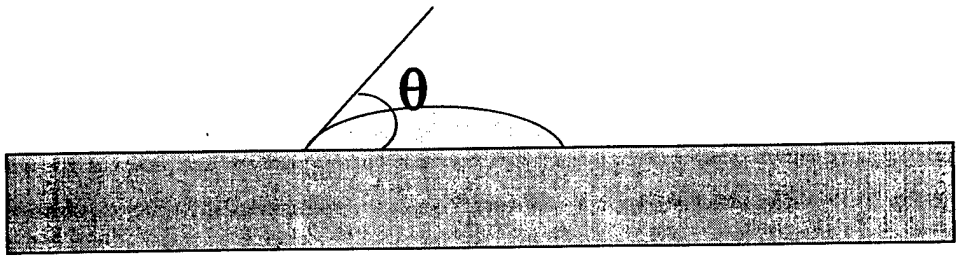


Figure 2. Contact angle of a liquid drop on a solid surface.

b. Ag Conductor Patterns

The conductivity of printed conductor patterns was characterized with a digital multimeter using either a two- or four-probe technique. In the early stage of this research, a 2-probe measurement was used to characterize the resistance of the Ag patterns. A 4-probe device was fabricated and used in the latter part of the research work. In the 4-probe measurement, a source current is past through the two outer probes while the voltage is measured from the two inner probes. Scanning electron microscopy (SEM) was used to investigate the microstructure of the conductor patterns, the interface between the silver metal and the polymer substrate, and the thickness of the printed silver conductor for conductivity determination.

The mechanical integrity of the reduced silver conductor was characterized by a folding test. Sample coupons with the printed conductor pattern were folded, either inward or outward, 180° along an axis perpendicular to the printed conductor lines. The folded samples were then pressed firmly along the folding line by hand. The physical integrity of the Ag conductor patterns was observed under an optical microscope. The electrical resistance of the printed Ag patterns across the folding axis was measured before and after folding. An adhesive tape test was used to characterize the adhesion of the printed conductor on polymer substrates. In the tape test, a piece of Scotch® tape was firmly adhered to the substrate with printed Ag patterns and then removed. The significance of the Ag pattern being pulled off the substrate was used as a measure for the adherence of the Ag pattern on the substrate. Electrical resistance of the Ag patterns was also measured before and after the tape test.

4 Results and Discussion

4.1 Precursor Solutions

The wetting of ink is critical to the formation of precise patterns on the substrate with high resolutions. It is undesirable for the ink to have low contact angles, because it would spread out on the substrate. On the other hand, a high contact angle, e.g. 90° or higher, is also undesirable, for the ink becomes non-wetting, or forms "beads," on the substrate. Therefore, a proper contact angle of the ink should be somewhere in the middle, say between 30 to 60°. The optimum contact angle of the ink to a specific substrate should be fine-tuned in the final stage of the ink development. In this Phase I work, preliminary exploration of the wetting properties of various solvents and silver nitrate precursor solutions on the three polymer substrates was performed.

The contact angles of neat DMAc and that of a 50 wt% $AgNO_3$/DMAc solution on the Upilex® substrate with different surface treatments are listed in Table 2. The contact angle of the neat DMAc on the Upilex® without any surface treatment was 2.8°. This small contact angle suggests that DMAc has a strong wetting ability to Upilex®. In fact, DMAc is a good solvent for the precursor (i.e., the polyamic acid form) of Upilex®.

The wettability of DMAc to Upilex® was further enhanced by bathing the polymer in a strong acid prior to the measurement of contact angles. This was probably due to a partial conversion of the surface polyimide to polyamic acid. The result was opposite by bathing the polymer in Windex® window cleaner. This might be related to the alkalinity (pH ~ 10) of the Windex® solution, despite the content of surfactants in the solution. The contact angle of the pure DMAc on Upilex® was significantly increased by the presence of silver nitrate. It seems that this effect was so prominent that the effect of surface treatments was no longer significant. An intuitive explanation for this is that the interaction between DMAc and silver nitrate has decreased the interaction between the solvent and the polymer.

The contact angle of pure DMAc and the 50%$AgNO_3$/DMAc solution on Kapton® and Kaladex® are summarized in Tables 3 and 4, respectively. Again, the DMAc wets both Kapton® and Kaladex® substrates well. However, the contact angles of both the solvent and the silver nitrate solution on the Kapton® and Kaladex® substrates are about twice as high as those on the Upilex® films. These results suggested that both Kapton® and Kaladex® have much lower surface energy than Upilex®. Table 5 compares the effect of two different solvents, DMAc and DMSO, on the contact angles of $AgNO_3$ solutions on all three polymers. The DMSO solution exhibited much higher contact angles on all three polymers than the DMAc solution, indicating weaker interfacial reactions between DMSO and the polymers.

It was noticed that electrostatic charges were present upon all polymer substrates, most prominently on the Kapton® films. Even though a Zerostat-3 static neutralizer was used to neutralize the charges, residual electrostatic forces remained. It is not clear at this time to what degree this has contributed to the errors of the contact angle measurements. Furthermore, dust wipes were used to clean the polymer substrates, but dust particles continued to be attracted to the films, which may have interfered with the solution adhesion to the substrates.

Table 2. Contact Angle of DMAc and Silver Nitrate/DMAc Solutions on Upilex®.

Polymer Substrate	**Surface Treatment**	**Liquid Tested**	**Contact Angle (degrees)**
Upilex ®	None	DMAc	2.8
Upilex ®	Concentrated HCl	DMAc	1.7
Upilex ®	Windex ®	DMAc	6.8
Upilex ®	None	50% $AgNO_3$/DMAc	15.5
Upilex ®	Concentrated HCl	50% $AgNO_3$/DMAc	18.3
Upilex ®	Windex ®	50% $AgNO_3$/DMAc	17.3

Table 3. Contact Angle of DMAc and a Silver Nitrate/DMAc Solution on Kapton®.

Polymer Substrate	Surface Treatment	Liquid Tested	Contact Angle (degrees)
Kapton ®	None	DMAc	7.0
Kapton ®	Concentrated HCl	DMAc	5.3
Kapton ®	Windex ®	DMAc	9.8
Kapton ®	None	50% $AgNO_3$/DMAc	33.0

Table 4. Contact Angle of DMAc and a Silver Nitrate/DMAc Solution on Kaladex®.

Polymer Substrate	Surface Treatment	Liquid Tested	Contact Angle (degrees)
Kaladex ® 1030	None	DMAc	8.3
Kaladex ® 1030	Concentrated HCl	DMAc	10.8
Kaladex ® 1030	Windex ®	DMAc	10.4
Kaladex ® 2000	None	DMAc	10.4
Kaladex ® 2000	Concentrated HCl	DMAc	4.0
Kaladex ® 2000	Windex ®	DMAc	7.9
Kaladex ® 1030	None	50% $AgNO_3$/DMAc	30.5
Kaladex ® 2000	None	50% $AgNO_3$/DMAc	35.0

Table 5. Contact Angle of $AgNO_3$ Solutions on Different Substrates

Polymer Substrate	Surface Treatment	$AgNO_3$/DMAc (50 wt%)	$AgNO_3$/DMSO (50 wt%)
Upilex ®	None	15.5	29.6
Kapton ®	None	33.0	39.3
Kaladex ® 1030	None	30.5	53.2
Kaladex ® 2000	None	35.0	46.0

Viscosity is one of the critical properties of the conductive ink for the inkjet printing process. As shown in Fig. 3, the measured viscosity of various silver precursor solutions increases with $AgNO_3$ concentrations. The viscosity for the 50 wt% $AgNO_3$/DMAc solution was 6.8 cP. Our communication with inkjet printer manufacturers indicated that the proper ink viscosity for inkjet printing should be 30 cP or less. The viscosity values of the $AgNO_3$/DMAc solutions are well within the suitable range for inkjet printing process. We expect that when other ingredients such as binder and filler are added to the ink formulation, the viscosity of the precursor solutions will further increase, but should stay within the operation range for inkjet printing applications.

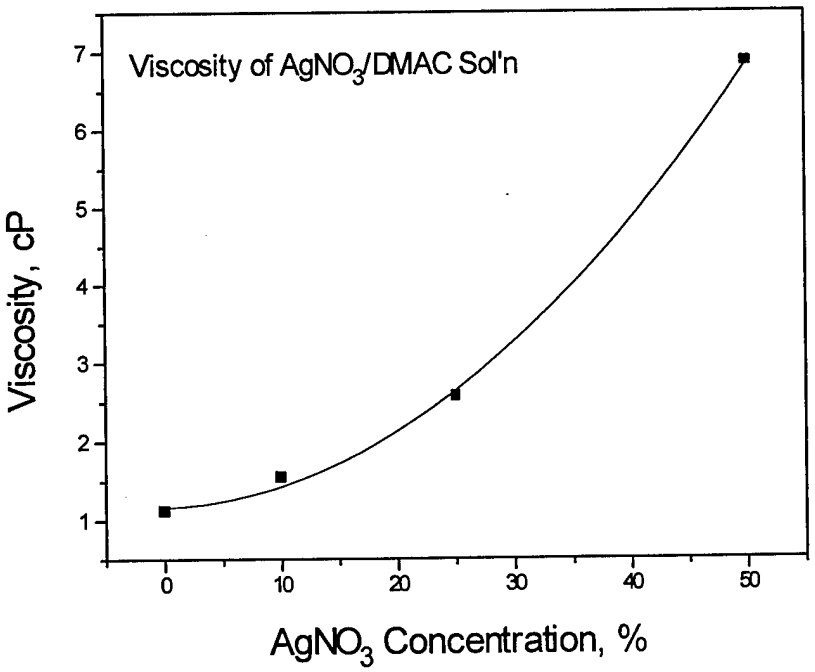


Figure 3. Viscosity of $AgNO_3$/DMAc solutions

4.2 Pattern Formation and Thermal Reduction of Precursor Solutions

Pattern formation of various silver nitrate solutions on the three polymer substrates was studied. The conductor patterns were created by the doctor-blading method or using a drawing pen to print the precursor solutions on the polymer films. The printed precursor patterns were than dried and thermally treated to give conductive metal patterns. In the initial experiment, samples of Kaladex® films deformed significantly when being heat-treated to temperatures of 250°C and above, suggesting that it did not have the thermal stability needed for fabricating flexible circuits using this processing scheme. Therefore, most research effort was focused on the two polyimide substrates. Silver nitrate solutions in DMAc with concentrations up to 50 wt% were patterned on Kapton® and Upilex® films, respectively. Examples of conductor patterns on both types of substrate materials are shown in Figure 4. The 10% solution spread out on both types of polymer substrates during drying and could not maintain the shape of the pattern. The 25% solution also spread out on the polymer films, but to a lesser extent than the 10% solution did. Both the 40 and 50% $AgNO_3$ solutions formed good patterns on the polymer films and the patterns maintained their shapes through out the thermal reduction process up to 400°C in air. The conductor patterns on different polymer substrates also behaved differently. The silver conductor patterns on the Kapton® films are uniform in both the appearance and the conductivity. On the other hand, conductor patterns on the Upilex® films appeared to have different phases. Certain areas of the conductor patterns on the Upilex® films showed bright silver color and good conductivity, while some other areas were dull gray with low conductivity or no measurable conductivity. The cause for this non-uniformity is not clear. The effects of $AgNO_3$ solution concentration on the conductivity of the Ag patterns on polyimide substrates are summarized in Table 6.

The effects of three different solvents (DMAc, NMP, and DMSO) used in the silver nitrate precursor solutions on the pattern formation and the conductivity of the Ag conductor patterns were also studied. The three precursor solutions were printed on Upilex® and Kapton® films, respectively, with a drawing pen and subsequently dried on a hot plate and heat-treated in a furnace to 300°C in air for 30 min. Samples of Ag patterns derived from these three precursor solutions are shown in Fig. 5. Sheet resistance data of the Ag patterns are listed in Table 7. All of the three precursor solutions exhibited good pattern formation capability, and the Ag patterns obtained also showed good conductivity on the Kapton® substrate. Sheet resistance data in Table 7 again indicated that conductor patterns formed on Upilex® were not uniform, with areas showing low or no conductivity. The three solvents did not show significant effects on either the pattern formation or the resistance of the patterns derived from the individual precursor. However, The precursor made with DMSO did exhibit slightly better pattern forming capability. Conductor patterns obtained from that solution also tended to be more consistent in conductivity.

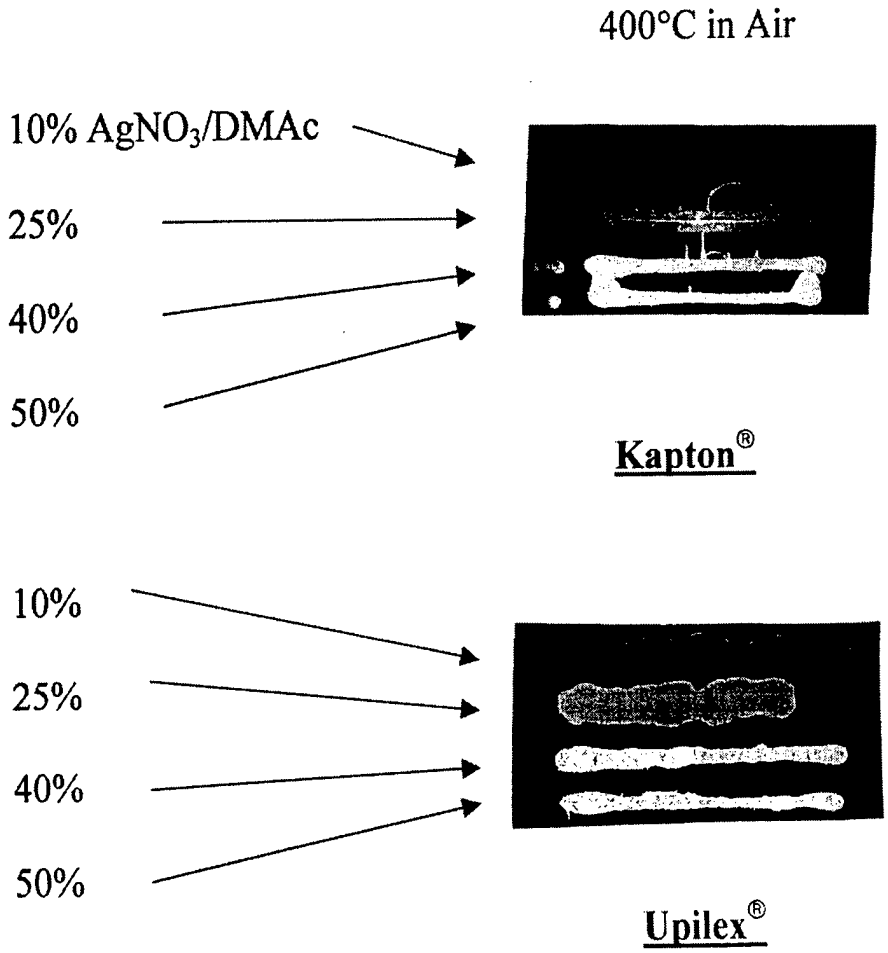


Figure 4. Ag conductor patterns formed from $AgNO_3$/DMAc precursor solutions of different concentrations on Kapton® and Upilex® substrates after heat treatment at 400°C in air for 30 min.

Table 6. Effects of $AgNO_3$ Concentration on the Conductivity of the Silver Pattern on Two Polyimide Substrates.

$AgNO_3$ in DMAc, wt. %	**Sheet Resistance, Ohm/□**	
	Upilex®	**Kapton®**
10	> 20M	> 20M
25	> 20M	> 20M
25	> 20M	355
40	> 20M	0.23
40	58	0.19
50	> 20M	0.10
50	0.35	0.25

Note: Samples were heat treated at 400°C in air. Resistance was measured with the 2-probe method.

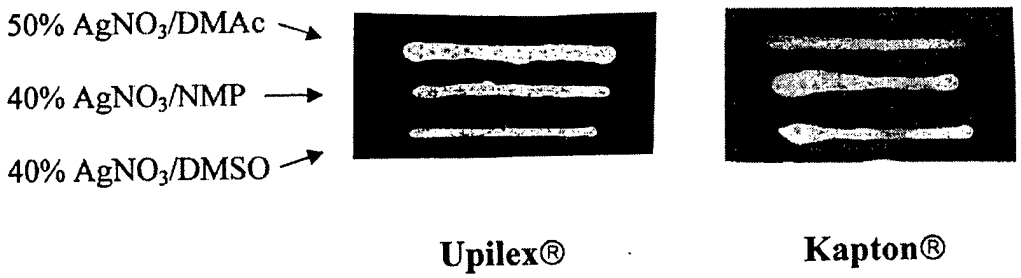


Figure 5. Ag conductor patterns derived from $AgNO_3$ solutions in different solvents. The patterns were printed on the substrate with a drawing pen and heat treated at 300 °C in air for 30 min.

Table 7. Conductivity of the Silver Conductor Patterns Prepared on Two Polyimide Substrates from $AgNO_3$ Solutions in Different Solvents.

Solvent	$AgNO_3$ Conc., wt%	Sheet Resistance, Ohm/□	
		Upilex®	Kapton®
DMAc	50	0.24	0.14
DMAc	50	58.3	0.23
NMP	40	1.49	0.16
NMP	40	162	0.28
DMSO	40	0.39	0.09
DMSO	40	4.22	0.11

Note: Samples were heat treated to 300°C in air for 30 min. Resistance was measured with the 2-probe method.

In the thermal reduction of the silver nitrate on polymer substrates, the solvent was first removed by evaporation at around 100°C. Upon further heating, silver nitrate melted at 212°C and decomposed at higher temperatures. A systematic study was conducted to identify the processing windows for the thermal reduction reactions. Samples were heat treated to different temperatures between 250 and 400°C either in air or under vacuum. After heat treatment, the conductor patterns were characterized with their physical appearance and conductivity. The effect of heat treatment conditions on the conductivity of the Ag patterns on Kapton® substrate is summarized in Figure 6, where all the Ag patterns were derived from a 50% $AgNO_3$ solution in DMAc. For samples heat-treated in air, the reduction of silver nitrate to silver metal occurred at a temperature as low as 250°C. The conductor patterns exhibited a silver color with good conductivity. Samples heat treated to higher temperatures did not show significant improvement in their conductivity. Samples thermally reduced under vacuum between 300 and 400 °C exhibited similar characteristics to those heat-treated in air. However, the conductor patterns obtained from heat-treatment at 250°C under vacuum were grayish in color and exhibited much lower conductivity. The result indicates that oxygen may play a role in affecting the thermal reduction of silver nitrate through the formation of thermally unstable silver oxide.

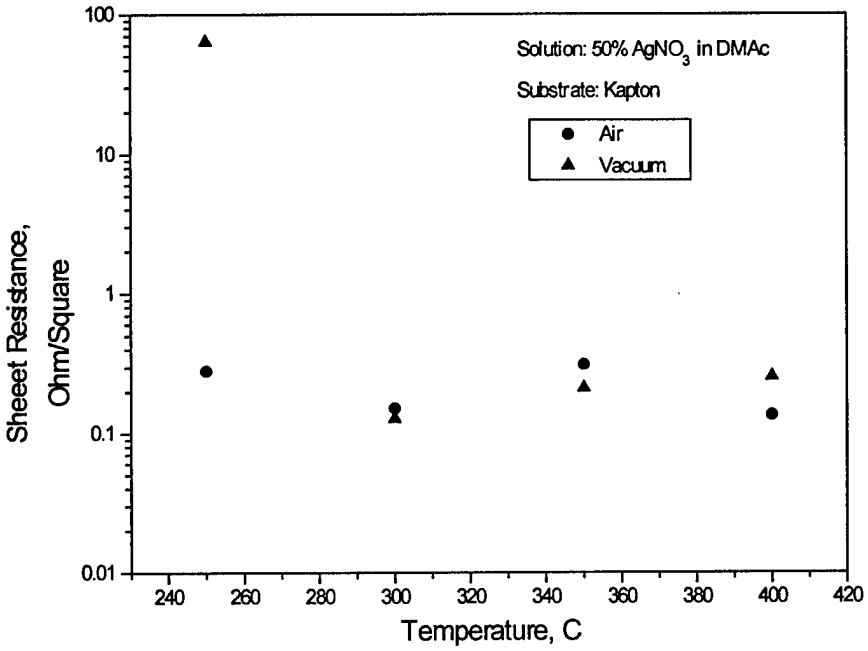


Figure 6. Effects of heat-treatment conditions on conductivity of Ag conductor patterns on Kapton® films. Resistance of the Ag patterns was measured with the 2-probe method.

4.3 Adhesion and Mechanical Integrity of Ag Conductor Patterns

Two approaches were investigated to enhance the adhesion and mechanical integrity of the Ag conductor patterns on polymer substrates. The first approach involved surface modification of the polymer substrates with a thin coating of the polyamic acid (poly[N',N'-(1,4-phenylene)-3,3',4,4'-benzophenonetetracarboxylic imide/amic acid], PAA). A-2 wt% polyamic acid/DMAc solution was applied to the surface of Upilex® and Kapton® coupons with a paintbrush. The polyamic acid coatings were dried on a hot plate at around 100°C. During the drying process, the polyamic acid solution became non-wetting on the Upilex® substrate. The coating shrunk into droplets on the surface of the Upilex® coupons and subsequently dried into scattered circular islands. Therefore, only Kapton® films were continued with PAA coating studies. Several different silver nitrate precursor solutions were printed on the PAA-coated Kapton® coupons, followed by heat treatment procedures described in the previous sections. The conductivity of Ag conductor patterns on the surface-modified Kapton® coupons are compared with those without surface modification in Table 8. It shows that the PAA coating improved the conductivity of Ag patterns prepare from low concentration $AgNO_3$ solutions.

Table 8. Effect of Polyamic Acid Coating on the Conductivity of the Silver Conductor Patterns on Kapton® films.

Solution	Sheet Resistance, Ω/□	
	No Coating	With PAA Coating
10% $AgNO_3$/DMAc	> 20M	> 20M
25% $AgNO_3$/DMAc	6.65	0.52
	2.20	0.46
40% $AgNO_3$/DMAc	0.24	0.15
	0.20	0.14
50% $AgNO_3$/DMAc	0.16	0.15
	0.16	0.13
40% $AgNO_3$/DMSO	0.09	0.10
40% $AgNO_3$/NMP	0.16	0.18

Note: Samples were heat treated at 300°C in air for 30 min. Resistance was measured with the 2-probe method.

The second approach to improving the adhesion between the Ag conductor pattern and the polymer substrate involved modification of silver nitrate precursor solutions by dissolving a modest amount of polyamic acid in the solution. Although polyamic acid is soluble in solvents such as DMAc and DMSO, it becomes insoluble with the presence of $AgNO_3$. Southward et al. developed a technique to incorporate silver acetate into polyamic acid solutions by chelating with 1,1,1-trifluoroacetylacetone (TFA) or 1,1,1,5,5,5-hexafluoroacetylacetone (HFA)[4,5]. However, the solubility of silver acetate in DMAc and DMSO with the chelating compounds is still limited. In this research, the two chelating agents were studied for their effectiveness in promoting the solubility of the polyamic acid in the 40 wt% $AgNO_3$/DMAc solution. PAA-modified Ag precursor solutions were prepared by adding different quantities of the chelating compound into the 40% $AgNO_3$/DMAc solution, as shown in Table 9. A small quantity (~ 1 ml) of a 12 wt% polyamic acid/DMAc solution was then slowly added to the chelated silver nitrate solution with stirring. The polyamic acid precipitated immediately in the silver nitrate solution and formed small pieces of a white solid. After stirring overnight at room temperature, the remaining solid was separated from the liquid by filtration. The clear filtrate was typically light brown in color. The PAA concentration in these solutions was not determined. However, the fact that the color of the precursor solutions became progressively darker from AgTFA1 to AgTFA3 suggested that more polyamic acid was dissolved in the solution when more TFA was add to form the silver-TFA complex.

Table 9. Composition of Chelated $AgNO_3$ Solutions with Dissolved Polyamic Acid.

Solution	$AgNO_3$ (g)	DMAc (g)	TFA (g)	HFA (g)
AgTFA1	4	6	1	--
AgTFA2	4	6	2	--
AgTFA3	4	6	3	--
AgHFA1	4	6	--	3

A matrix experiment was designed to evaluate the effects of different precursor solutions and processing conditions on the properties of Ag conductor patterns on the two types of polyimide substrates. The matrix is shown in Table 10 along with the sheet resistance of the Ag conductor patterns produced from these processing conditions. As it has been shown in the previous section, Ag conductor patterns on unmodified Upilex® films were non-uniform, and in many cases, were not conductive. Moreover, the diluted PAA solution did not wet Upilex® well at the room temperature. However, the PAA solution could be brushed on a Upilex® substrate when it was hot. With the coating, both the uniformity and conductivity of the conductor improved significantly on Upilex® substrates.

Ag conductor patterns derived from the 40 wt% $AgNO_3$/DMSO solution exhibited excellent conductivity on Kapton® substrates, with or without the polyamic acid coating. The conductor patterns also exhibited relatively good mechanical integrity and adhesion to the substrate. There were no sign of cracking and chipping under gentle handling and manipulations. The Ag patterns, however, could be pulled off easily with a piece of Scotch® tape in the tape test.

The precursor solutions containing chelating agent and PAA exhibited good pattern formability on hot (~120°C) Kapton® substrates. However, the two chelating agents seemed to increase wetting of the precursor solutions on polyimide substrates. The printed pattern of AgTFA3 and AgHFA1, which had a higher concentration of the chelating agents, tended to spread out and became a little wider than their original sizes. When precursor solutions were printed on unmodified Kapton® film at room temperatures, the solution became non-wetting during drying, and separated into droplets. When printed at 120°C, the PAA-modified precursor solutions generated conductor patterns with good electrical conductivity on Kapton® substrates. However, on unmodified Kapton® substrates, the Ag patterns did not fare well in the tape test. Most of the patterns were pulled off by the Scotch® tape.

Table 10. Effects of PAA Surface Modification and PAA-Containing $AgNO_3$ Precursor solutions on the Conductivity of Ag Patterns on Upilex® and Kapton® Substrates.

Precursor Solution	Sheet Resistance[+], Ω/□					
	No PAA Coating Substrate T = 20°C		No PAA Coating Substrate T = 120°C		PAA Coating Substrate T = 120°C	
	Upilex®	Kapton®	Upilex®	Kapton®	Upilex®	Kapton®
40 wt% $AgNO_3$/DMSO	0.10**	0.04	0.07**	0.04	2.0	0.05
AgTFA1	> 40M	0.20	0.14**	0.05	6.9	0.07
AgTFA2	0.40**	--*	> 40M	0.06	0.5	0.04
AgTFA3	> 40M	--*	> 40M	0.12	0.8	0.05
AgHFA1	1.1**	--*	0.25**	0.05	1.5	0.07

Note: +) Resistance data are average values measured from several samples.
*) Precursor solution was non-wetting on the substrate, no defined pattern was formed.
**) Conductor patterns were not uniform in conductivity. Resistance values were measured from areas that showed conductivity.
++) All of the samples were heat-treated in air at 350°C for 1 hr. Resistance was measured with the 4-probe method.

The Ag conductor patterns obtained from printing PAA-modified precursors on PAA-modified substrates at an elevated temperature (~120°C) fared the best in the tape test. Figure 7 shows SEM micrographs of the Ag conductor pattern samples on PAA-coated Kapton® and Upilex® substrates. It is apparent that the bottom part of the Ag conductor layer was embedded in the imidized PAA coating, which is indistinguishable from the polyimide substrate. The partial embedment of the Ag conductor layer in the PAA coating as well as the polyamic acid binder in the precursor solution imparted enhanced adhesion and mechanical integrity to the conductor patterns on both types of polyimide substrates. The Ag conductor patterns derived this manner survived the tape test with minimal damages and retained high electrical conductivity, as shown in Table 11. Conductor patterns on the PAA-coated Upilex® substrates exhibited stronger adhesion than those on the PAA-coated Kapton® substrates. Figure 8 shows the microstructure of the conductor/substrate interface of samples that survived the tape test. The sample shown in Figure 8(a) was on a PAA-coated Upilex® substrate, and that in Figure 8(b) was on a coated-Kapton® substrate. While the conductor on the Upilex® film was mostly intact after the tape test, that on the Kapton® film showed some indication of delamination.

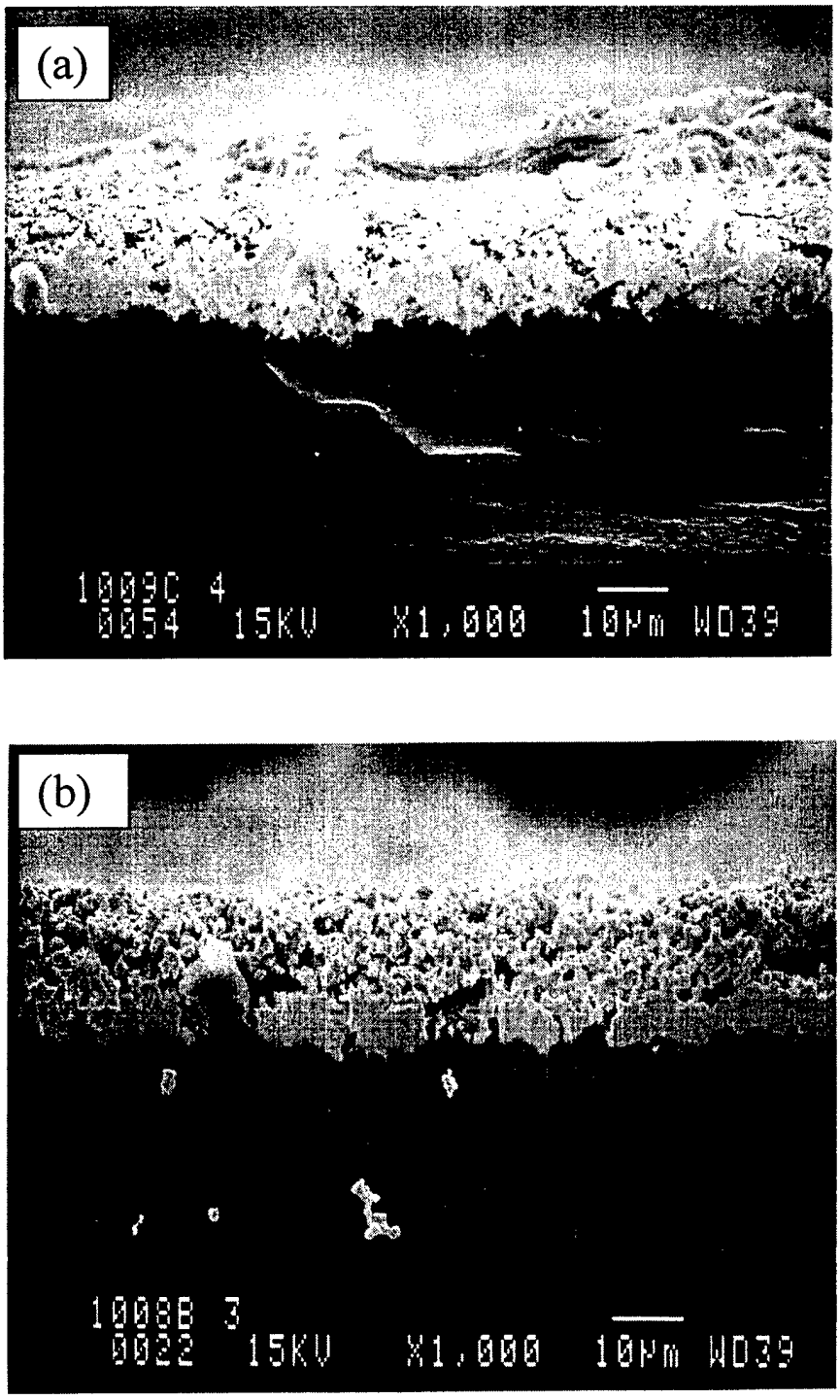


Figure 7. Cross-section SEM micrograph of Ag conductor pattern on (a) Upilex® and (b) Kapton® substrates.

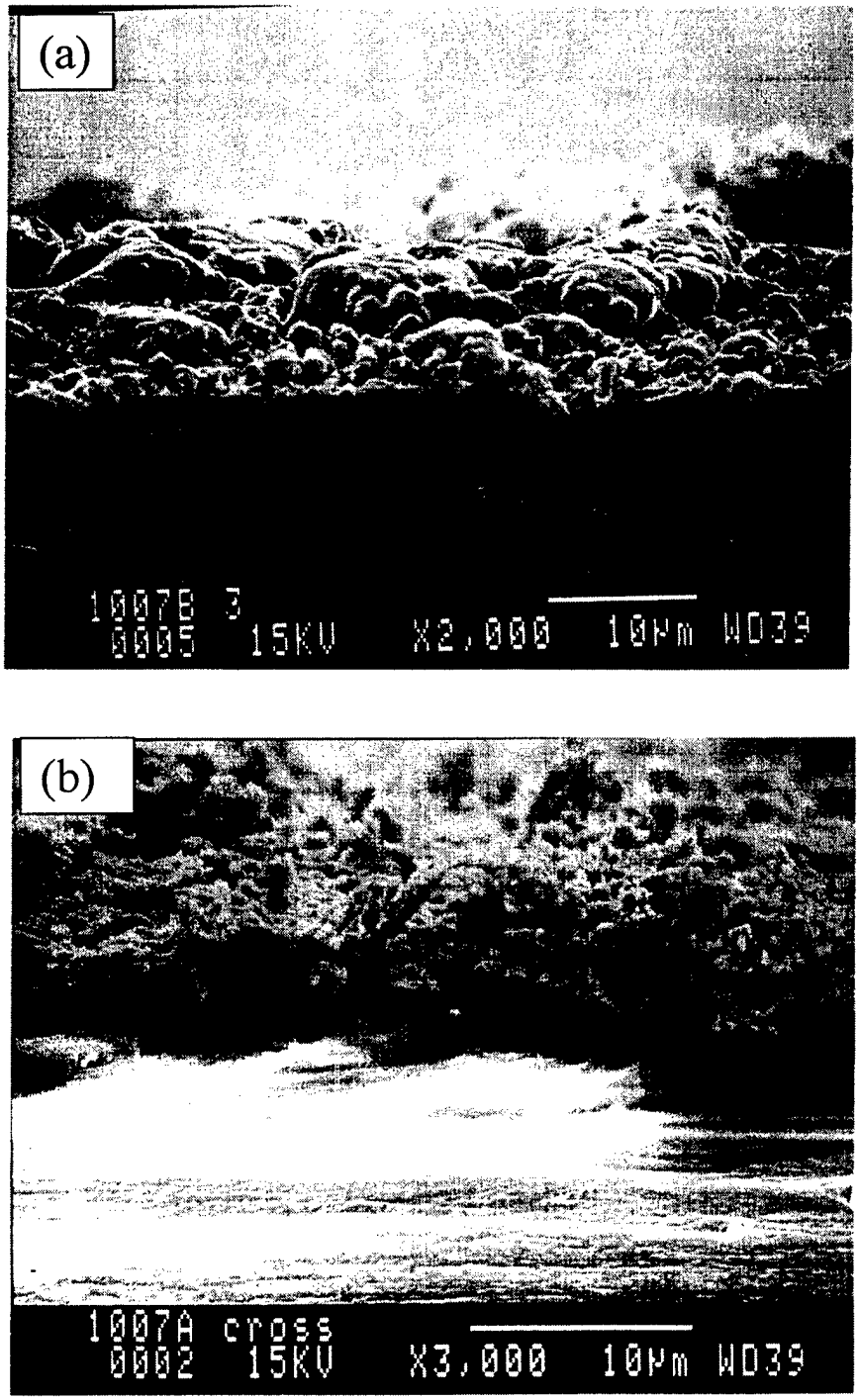


Figure 8. Cross-section SEM micrograph of Ag conductor pattern on (a) Upilex® and (b) Kapton® substrates after the tape test.

Results of outward and inward folding tests for conductor patterns produced from different precursors and processing conditions are summarized in Tables 12 and 13, respectively. In general, the Ag conductor patterns fared better in the outward folding test than in the inward folding test. The former subjected to a tension while the latter subjected to a compression mechanical deformation. In most cases, the conductor patterns did not reveal any obvious physical damages under the optical microscope when they were folded outward 180° and pressed firmly with fingers. The increase in sheet resistance of the conductor patterns across the folding axis, however, suggested that micro-cracks had occurred due to the folding test. On contrary, the inward folding caused cracks and delaminations of the conductor patterns along the folding axis. As a result, a much bigger resistance change occurred across the folding line. It should be noted that the conductor patterns subjected to a much more severe deformation in these folding tests than those in the standard flexibility test used by the industry. Therefore, the dramatic resistance change in some conductor patterns was not considered to be lack of flexibility. In both folding tests, the Ag patterns obtained from the PAA-modified precursors exhibited much smaller changes in resistance than those from the unmodified $AgNO_3$/DMSO precursor solution. In addition, the added PAA coating on the substrate did not show appreciable effect on the performance in the folding tests. Results suggested that the incorporation of PAA in the precursor solutions enhanced the mechanical integrity of Ag conductor patterns on polyimide substrates.

The silver conductor patterns generated from the precursor solutions on PAA-modified Kapton® substrates typically exhibited a sheet resistance in the range of 0.03 ~ 0.07 Ω/square. The addition of the chelating agent and polyamic acid to the precursor formulation seemed to have little effect on the resistance of the resultant conductor patterns. The conductor patterns obtained in this study were generally a Ag layer of 10 to 20 μm thick (as shown in Figure 7). The calculated resistivity of the conductor patterns was in the range of 10^{-4} ~ 10^{-5} Ω-cm. Although these values are about one order of magnitude higher than that of pure silver at room temperature, they are compatible with those of the state-of-the-art thick film conductors currently used in the electronic packaging industry [6,7].

Table 11. Resistance of Ag Conductor Patterns Derived from PAA-Modified Precursor Solutions on PAA-Modified Polyimide Substrates, Before and After Tape Test.

Precursor	**Sheet Resistance, Ω/□**					
	Kapton®			**Upilex®**		
	Sample #	**Before**	**After**	**Sample #**	**Before**	**After**
AgTFA1	1007A1	0.045	0.077	1007B1	0.41	7.69
AgTFA2	1007A2	0.036	0.100	1007B2	0.038	0.046
AgTFA3	1007A3	0.036	0.053	1007B3	0.037	0.046
AgHFA1	1007A4	0.038	0.047	1007B4	0.054	0.055

Note: Samples were heat-treated to 350°C in air for 1 hr. Resistance was measured using the 4-probe method.

Table 12. Outward Folding of the Ag Conductor Patterns Derived from Different Precursor Solutions under Different Processing Conditions on Kapton® Substrate.

Sample #	Precursor Solution	PAA Coating	Sheet Resistance, Ω/□		Change
			Before Bending	After Bending	
21A1	40 wt% $AgNO_3$/DMSO	No	0.026	0.042	+ 62%
102B1	40 wt% $AgNO_3$/DMSO	Yes	0.053	0.090	+ 70%
21B2	AgTFA1	No	0.082	0.104	+ 27%
102B2	AgTFA1	Yes	0.041	0.052	+ 27%
102A3	AgTFA2	Yes	0.049	0.047	- 4%
102B4	AgTFA3	Yes	0.036	0.038	+ 6%
102B5	AgHFA1	Yes	0.067	0.080	+ 19%

Note: Samples were heat-treated to 350°C in air for 1 hr. Resistance was measured using the 4-probe method.

Table 13. Inward Folding of Ag Conductor Patterns Derived from Different Precursor Solutions under Different Processing Conditions on Kapton® Substrate.

Sample #	Precursor Solution	PAA Coating	Sheet Resistance, Ω/□		Change
			Before Bending	After Bending	
21B1	40 wt% $AgNO_3$/DMSO	No	0.17	5.26	+ 2,994%
102A1	40 wt% $AgNO_3$/DMSO	Yes	0.05	0.68	+ 1,360%
21A2	AgTFA1	No	0.34	1.41	+ 315%
102B2	AgTFA1	Yes	0.06	0.35	+ 483%
102B3	AgTFA2	Yes	0.04	0.34	+ 750%
102B4	AgTFA3	Yes	0.05	0.15	+ 200%
102B5	AgHFA1	Yes	0.03	0.25	+ 733%

Note: Samples were heat-treated to 350°C in air for 1 hr. Resistance was measured using the 4-probe method.

5. Conclusions

This STTR Phase I research investigated the feasibility of a processing scheme leading toward the fabrication of flexible printed circuits with computer-aid design tools using inkjet printing technology. This processing scheme comprises three basic steps: (1) application of a metal precursor solution to form the pattern of a desired pattern on a polymer substrate, (2) evaporation of the solvent of the metal precursor from the substrate, and (3) thermal decomposition of the metal precursor to form the conductive circuit.

Precursor solutions of silver nitrate in different organic solvents were evaluated for their wetting ability on three commercial polymer films currently used in the flexible circuits manufacturing. Solutions containing 40 to 50 wt% $AgNO_3$ exhibited good pattern forming ability on two of the polyimide films, Kapton® and Upilex®. The viscosity of these solutions (5 ~ 7 cP) was well within the proper range for inkjet printing applications. Ag conductor patterns on polyimide substrates with high conductivity were produced by heat treatment of printed precursor patterns to 300°C in air.

Two approaches were investigated for improving the adhesion and mechanical integrity of the Ag conductor on polyimide films. The first involved the modification of polymer substrates with a polyamic acid coating, while the second involved the addition of a polyamic acid binder in the precursor solution. Combination of these two approaches generated Ag conductor patterns with excellent electrical conductivity and good mechanical performance in both the tape and folding tests. The resistivity of the Ag conductor was in the range of 10^{-4} to 10^{-5} Ω-cm, and was at the same level as that of the state-of-the-art thick film technology.

These results successfully demonstrated that this processing scheme is feasible for fabricating next-generation flexible printed circuits using the inkjet printing method. This novel processing scheme takes full advantage of the current computer-aided design and manufacturing technologies, and has potential to be extended for fabricating multiple-layer circuits as well as complex circuits on a contour surface. In addition, this process is material saving and environmentally benign. A wide-range of lightweight, high-performance flexible circuits can be prepared for applications in consumer electronics, telecommunication devices, automobiles and space and aerospace vehicles.

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