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A PROCESS FOR 1mm POLYANILINE/NOVOLAC LINES

BY PHOTOLITHOGRAPHY

A Thesis

Presented to

The Faculty of the Department of Chemical and Materials Engineering

San Jose State University

In Partial Fulfillment

of the Requirements for the Degree

Master of Science

by

Yuh-jaw (Roger) Luo

December 1999

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ABSTRACT

A PROCESS FOR 1mm POLYANILINE/NOVOLAC LINES BY PHOTOLITHOGRAPHY

by Yuh-jaw (Roger) Luo

This study demonstrated the feasibility of patterning a Polyaniline/Novolac coating by photolithography. The spin coating, baking, exposure and development conditions were developed and applied to glass slides, bare and oxidized silicon wafers. The coatings were unevenly distributed on the substrate, and decreased in thickness towards the edge. The coating thickness averaged 3 - 4 μm . The coating surface was rough, approximately $\pm 1.5 \mu\text{m}$, due to the PANI particle size. The coating adhesion varied with the substrate surface roughness and was best on oxidized silicon wafers. PANI/Novolac coatings with 30 - 35 wt % PANI provided the best combination of conductivity and photoresponse.

The conductivity of 1mm 30 wt % PANI/Novolac pattern lines was 0.00076 S/cm on an oxidized silicon wafer. The patterns were continuous lines, and not erased by touching and wiping. The pattern edge was straight, but rough with a variation of 50 μm . Some PANI particles remained in the exposed regions.

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The last, but not the least. To my dearest Grandmom who is living above the sky, " I made it!"

TABLE OF CONTENTS

LIST OF FIGURES	vi
LIST OF TABLES	x
1.0 INTRODUCTION	
1.1 Conductive Polymer	1
1.2 Photoresist Coatings and Photoreaction	3
1.3 Photolithography	6
1.4 Objectives	10
2.0 LITERATURE REVIEW	
2.1 <i>Photolithographic Technique for Patterning Spin-coated Polyaniline Films</i>	11
2.2 <i>Water Soluble Conducting Polyanilines: Application in Lithography</i>	15
2.3 <i>Deposition of Conducting Polyaniline Patterns with the Scanning Electrochemical Microscope</i>	17
2.4 <i>Microfabrication of Interdigitated Polyaniline/Polymethylene Patterns on a Gold Surface</i>	19
2.5 <i>Summary</i>	22
3.0 EXPERIMENT	
3.1 Preparation and Process	
3.1.1 <i>Preparation of Formulation</i>	23
3.1.2 <i>PANI/Novolac Coatings</i>	24
3.1.3 <i>Patterning Process</i>	26
3.2 Characterization	
3.2.1 <i>Electrical Properties</i>	30

3.2.2	<i>Physical Properties</i>	33
4.0	RESULTS AND DISCUSSION	
4.1	Preparation of Formulation	34
4.2	Spin Coating Method	
4.2.1	<i>Single-Speed Coating Method</i>	35
4.2.2	<i>Multiple-Speed Coating Method</i>	37
4.3	Characteristics of Coatings through a 2-stage Method	42
4.4	Patterning Process	
4.4.1	<i>Prebaking</i>	50
4.4.2	<i>Exposure and Development</i>	50
4.4.3	<i>Conductivity Recovery</i>	56
4.5	Properties of 1 mm 30 wt % PANI/Novolac Lines	
4.5.1	<i>30 wt % PANI/Novolac Lines on Glass Substrate</i>	58
4.5.2	<i>30 wt % PANI/Novolac Lines on Silicon Wafers</i>	64
4.5.3	<i>30 wt % PANI/Novolac Lines on Oxidized Silicon Wafers</i>	69
4.5.4	<i>Comparison with Literature</i>	72
5.0	CONCLUSION AND FUTURE WORK	74
	REFERENCES	76
	APPENDIX	78

LIST OF FIGURES

Figure 1-1.	Patterns made by (a) positive photoresists and (b) negative photoresists ^[7]	4
Figure 1-2.	Chemical structure of Novolac Resin ^[8]	5
Figure 1-3.	Chemical reaction of Diazonaphthoquinone with UV light ^[8]	5
Figure 1-4.	A typical photolithography process (Metallization)	9
Figure 2-1.	Schematic diagram of photolithography procedure	12
Figure 2-2.	Patterned polyaniline film on a gold-coating glass substrate ^[12]	13
Figure 2-3.	Schematic diagram of a charge flow transistor (CFT) device	14
Figure 2-4.	Surface profile scan across a CFT device ^[12]	14
Figure 2-5.	Template synthesis of water-soluble polyaniline ^[13]	16
Figure 2-6.	One μ m conducting polyaniline lines in a 0.75 μ m thick film patterned by E-beam irradiation ^[13]	16
Figure 2-7.	Illustration of the SECM polyaniline deposition process	17
Figure 2-8.	A microscope image of a PANI pattern deposited on a Au substrate using a 10 μ m Pt tip electrode ^[15]	18
Figure 2-9.	Fabrication of patterned polymethylene-polyaniline film ^[16]	19
Figure 2-10.	A SEM micrograph of polyaniline polymethylene patterns on gold ^[16]	21
Figure 3-1.	Experiment flow chart	24
Figure 3-2.	The patterns on the mask	27
Figure 3-3.	The schematic of a 4-point probe	31
Figure 3-4.	The design of the conductivity reference locations on a coating	32
Figure 4-1.	A photography (200X magnification) of P-40/glass showing the "sea waves"	36
Figure 4-2.	Coatings produced by two multiple-speed coating methods	38
Figure 4-3.	A microscope photograph of a P-30/glass coating (200X magnification)	40
Figure 4-4.	Profilometer traces for three coatings produced (the 2-stage method)	44
Figure 4-5.	Thickness distribution of P-27.5, P-29, P-30, P-31, P-35, and P-40 coatings on glass substrates (2-stage method)	45

Figure 4-6.	The profilometer trace for a P-30 coating (2-stage method)	47
Figure 4-7.	The profilometer trace for the glass surface	47
Figure 4-8.	Photographs (200X magnification) of (a) the edge of the photoresist pattern, and (b) the edge of the laser-printer print used as the exposure mask	54
Figure 4-9.	Conductivity and photoresponse of the PANI/Novolac coatings (2-stage method)	55
Figure 4-10.	A photograph of the P-30/glass patterns	60
Figure 4-11.	A photograph of the 1mm P-30 line on a glass substrate (50X magnification)	61
Figure 4-12.	A Photograph of the 1 mm 30 wt % PANI/Novolac line on a glass substrate (200X magnification)	61
Figure 4-13.	Profilometer traces for (a) a 1mm P-30 line, (b) a P-30 line, and (c) a 1mm pure photoresist line on glass substrates	63
Figure 4-14.	A photograph of 1mm PANI/Novolac lines on a bare silicon wafer	66
Figure 4-15.	A 1mm P-30 line on a silicon wafer (50X magnification)	67
Figure 4-16.	The edge of a 1mm P-30 line on a silicon wafer (200 magnification)	67
Figure 4-17.	The profilometer traces for (a) a P-30/Si coating, (b) a 1mm P-30/Si line surface, and (c) a bare silicon wafer surface	68
Figure 4-18.	A profilometer trace for an oxidized silicon wafer surface	70

LIST OF TABLES

Table 1-1.	Examples of conducting polymers ^[1]	2
Table 1-2.	Two forms of polyaniline	3
Table 4-1.	Summary of compositions of the formulations and the respective coatings	34
Table 4-2.	Measured resistance of the coatings on glass substrates through the single-speed coating methods.	37
Table 4-3.	Characteristics of coatings prepared by the two multiple-speed coating methods	41
Table 4-4.	The conductivity and thickness of P-29, P-30, P-31, P-35, P-40 coatings through the 2-stage method	49
Table 4-5.	Summary of photoresponse of the PANI/Novolac coatings	51
Table 4-6.	Effect of the prebake conditions on P-30 coatings	52
Table 4-7.	The conductivity change of the P-30 pattern after an acid treatment	57
Table 4-8.	Process for 1mm 30wt% PANI/Novolac lines on a glass substrates	59
Table 4-9.	The properties of 1mm P-30 line on glass substrate	62
Table 4-10.	Process for 1mm P-30/Si lines	65
Table 4-11.	Properties of 1mm P-30/Si line	66
Table 4-12.	The conductivity of P-30 coatings and patterns on an oxidized silicon wafer	71
Table 4-13.	A comparison of P-30 coatings and 1 mm P-30 lines on a glass substrate and an oxidized silicon dioxide wafer (center region)	71

1.0 INTRODUCTION

1.1 Conductive Polymer

Polymers that have inherent conductivity have been intensely studied in the past two decades for their potential applications as conductors. The major applications of conductive polymers are for use in rechargeable batteries, microelectronics, power equipment, and microtools. Conductive polymers are plastics with free electrons that are capable of carrying charges. Their conductivity can range from 10^{-5} to 10^4 Siemen/meter. Conductive polymers have some advantages over traditional metal conductors: ease of processing, light weight, and variable conductivity. In addition, conductive polymers have less an environmental impact than some metals, e.g., lead, and are corrosion resistant.

Conductive polymers can be divided into two classes: inherent conductive polymers (ICP) and filled polymers. Examples of polymers with good conductivity in the family of ICPs are polyaniline (PANI), poly phenylene-vinylene, polypyrrole, poly thienylene-vinylene, and polythiophene. The structures of these polymers are shown in Table 1-1^[1].

The conductivity of polymers usually increases with temperature. As the temperature increases above 200°C, however, most polymers start to decompose and lose conductivity. The conductivity of polymers can be controlled through preparation and handling procedures.

PANI is the most environmentally stable of all the conductive polymers. Most conducting polymers will lose their conductivity at ambient temperature. PANI has been applied for use in some commercial products ^[2], such as LEDs, rechargeable batteries,

surface treatments for corrosion protection ^[3], and printed circuit boards ^[4].

Table 1-1. Examples of Conducting Polymers. ^[1]

<u>Polymer</u>	<u>Structure</u>	<u>Charge / Monomer</u>	<u>Conductivity, S/cm</u>
Polypyrrole		0.25 - 0.33	100 - 400
Polythiophene		0.05 - 0.15	1 - 20
Polyphenylene		0.2 - 0.4	100 - 500
Polyaniline		0.025 - 0.5	0.1 - 10
Polyacetylene		0.05 - 0.2	100 - 1000

PANI can be represented by the general formula: $-[(B-NH-B-NH)_x(B-N=Q=N)_{1-y}]_n$, where B denotes a benzenoid reduced unit and Q denotes a quinoid unit. There are four different forms of PANI. Two of these forms are shown in Table 1-2. The emeraldine salt form is conductive and the emeraldine base form is non-conductive.

Of concern in applying PANI is its poor solubility. PANI is effectively insoluble in common organic solvents. Because of this thermal insolubility, PANI is difficult to process and has poor mechanical properties. It is practically impossible to dissolve the doped (oxidized) high molecular weight emeraldine salt (PANI) in common non-polar or even weakly polar organic solvents. So far, N-methylpyrrolidinone (NMP) has proved to

be the most suitable solvent for PANI ^[5]. An extensive discussion of the dissolution and dispersion of the conducting PANI is presented by B. Wessling ^[6].

Table 1-2. Two forms of polyaniline.

1.2 Photoresist Coatings and Photoreaction

Photoresist coatings, "photoresists", are polymer materials that react chemically when exposed to light. Commercial photoresists are available as viscous blends, which are classified as either positive or negative. The photolithography procedure for both classifications is exactly the same. However, the images resulting from the photolithography procedure are opposites. As shown in Figure 1-1(a), the image made from a positive photoresist is a positive copy of the mask pattern, and the exposed areas are

removed while the unexposed areas of the coating remain. In the VLSI and ULSI industry, the positive photoresist is widely used since it produces better resolution. Positive photoresists are preferred to achieve patterns smaller than $3\text{ }\mu\text{m}$. For a negative photoresist, the exposed areas remain and give a negative image of the mask pattern, as shown in Figure 1-1(b). Negative photoresists are used in newspaper printing and some printed circuit board applications.

Figure 1-1. Patterns made by (a) positive photoresists and (b) negative photoresists.^[7]

A positive photoresist has four primary components: Novolac resin, 1,2-Diazonaphthoquinone, dyes and a gas-like solvent. Novolac Resin provides mechanical strength to the photoresist film. It dissolves slowly in alkaline developers, such as

aqueous NaOH. Its chemical structure is represented by Figure 1-2.

Figure 1-2. Chemical structure of Novolac Resin.^[8]

1,2-Diazonaphoquinone is photoreactive and reduces the rate of dissolution of Novolac resin in alkaline solutions. When the photoresist film is exposed to UV light, 1,2-diazonaphoquinone transforms to an indene carboxylic acid via the ketene intermediate, as shown in Figure 1-3. This indene carboxylic acid dissolves readily in alkaline solutions and therefore accelerates the rate of dissolution of the resin by a few hundred times^[8]. The dyes in photoresists are usually red, and are used to reduce the undesired exposure caused by the reflection of UV light.

Figure 1-3. Chemical reaction of Diazonaphoquinone with UV light.^[8]

Most early negative photoresists consisted of polymeric organic materials, such as poly(vinylcinnamate), which has long-chain molecules. Irradiation of these molecules by an energetic beam results in bonding or cross-linking of adjacent polymer chains, which increases the average molecular weight. These materials are referred to as cross-linking photoresists. In more recently developed negative photoresists, cross-linking is done with photogenerated reactive species. These photoresists are chemically inert synthetic polyisoprene rubbers, typically *cis*-poly-isoprene, in combination with a bisazide cross-linking component, which is photoreactive. These photoresists are readily soluble in an aromatic solvent before exposure to UV light. However, the characteristic of cross-linking negative photoresists results in ragged edges, or a loss of pattern fidelity that makes them unsuited for patterns less than $2\ \mu\text{m}$. Also, negative photoresists can only be removed with great difficulty once they have been exposed to UV light. Consequently, optical printing techniques have turned to positive photoresists for VLSI and ULSI applications.

1.3 Photolithography

Lithography is a technology that uses photoreactive materials and an etching process to produce a pattern on a thin film. This technology is widely used in the semiconductor industry to manufacture electronic circuits. Currently, it is the only practical method for making copper and aluminum inner wires in electronic devices, and, therefore, lithography is the key technology in the manufacture of these electronic devices. The

characteristics of the lithography processes determine the dimensions of the resulting device and will affect the quality, yield and cost of the product ^[9].

The stages of the lithography process can be summarized as shown in Figure 1-4. The process in the figure represents the generation of an inner wire in an electronic device, and is shown here only as an example using a positive photoresist. The steps are as follows.

1. Metallization: A thin layer of metal, such as copper or aluminum, is deposited on a substrate by evaporation, sputtering or electroplating.
2. Coating: A thin film of photoresists is coated evenly on the metal layer through spin-coating, dipping or other methods. Spin coating is the most widely used, because it is simple and the film thickness can be controlled by the spin speed.
3. Prebake (or softbake): The specimen is heated at temperatures of approximately 90 to 100 °C. Heating times range from 30 seconds on a hotplate to 30 minutes in an oven. The function of this step is to drive off most of the solvent from the photoresist. The dissolution rate in the developer will be highly dependent on the solvent concentration in the final photoresist. Generally, shorter times or lower temperature softbakes lead to an increased dissolution rate in the developer and so to a higher sensitivity, but at the cost of lower contrast ^[10].
4. Exposure: Selected areas of the photoresist are exposed to light through a mask. Light sources in lithography range from the near UV to the deep UV. E-beam, I-beam and X-ray irradiation are some newer sources being used. A mask is a transparent plate with a chrome pattern on it. The most common material used for masks is glass. A

mask is usually slightly larger than the substrate (or the wafer). A mask that is smaller than the substrate is called a reticle.

5. Development: The exposed and unexposed regions of a photoresist have very different dissolution rates in alkaline solutions such as NaOH. A pattern is created in the photoresist layer by preferentially dissolving away the more soluble regions. After exposure to light and development, the image or structure on the positive photoresist will be the same as the pattern of the mask, while the image or structure on the negative photoresist will be the reverse pattern of the mask.
6. Postbake (or hardbake): The film is next heated to remove the developer solvent and harden the photoresist against further energetic processes such as plasma etching. This step also promotes the film adhesion to the substrate.
7. Etching: The exposed metal is etched away by plasma while the metal under the photoresist pattern is protected from the plasma and remains. In this step, the pattern of the photoresist is transferred to the metal layer.
8. Stripping: The unexposed photoresist is removed by a chemical solvent such as acetone or methylethylketone. For these solvents to be effective they must be applied at approximately 80°C. For personnel safety reasons, 1-methyl-2-pyrrolidinone is used in addition to proprietary stripping solutions.

Currently, the UV light system is the most common optical printing method. It was believed to have a minimum size limitation of 0.2 μm , due to the wavelength of UV light (diffraction effects)^[11]. This limitation has now been reduced to 0.18 μm in productions using high numerical aperture lenses, deep UV source and phase contrast masks. It seems

unlikely the technology will allow for further extension. If feature sizes are to be scaled to $0.1\ \mu\text{m}$ or below, new lithographic techniques must be developed. These new techniques, using a very short wavelength energy source, such as an electron beam, X-ray or ion beam(s), are collectively called nonoptical lithography^[11]. At the present time, E-beam lithography can achieve feature dimensions as small as $0.15\ \mu\text{m}$. More development is needed before it can be used for industrial purposes.

Figure 1-4. A typical photolithography process. (Metallization)

1.4 Objectives

With its advantages of light weight, variable conductivity, and biodegradability, PANI has many potential applications. However, its poor solubility limits its use in pattern processing for use in microelectronic applications. The motivation for this thesis work is to expand the application of PANI for use in UV light patterning. Instead of the dissolution of PANI in solvents, this study will develop a procedure for generating patterns based on the dispersion of PANI in solvents.

The objective of this study is to demonstrate that a thin film of a PANI/Novolac formulation, which was applied from PANI dispersed in a commercial photoresist solution, can be patterned with UV light. The composition, dispersion quality, electrical conductivity, edge definition, and mechanical properties of the pattern will be determined.

2.0 LITERATURE REVIEW

2.1 A Photolithographic Technique for Patterning Spin-coated Polyaniline Films

C. Di Bartolomeo ^[12], *et al* demonstrated that polyaniline films could be deposited by spin coating and used photolithography techniques to pattern the films.

Polyaniline was synthesized by reacting a solution of NMP with excess ammonium persulphate. The reaction product was recovered as a filter cake, worked with 33% aqueous ammonia solution (to deprotonate the polyaniline), then dried in a vacuum at 60°C to give the emeraldine base form of polyaniline in approximately 90% yield. A solution of PANI/NMP, 6% by weight, was made, and centrifuged at 20,000 rpm for 10 minutes to render the solution homogeneous, then centrifuged twice for 1 hour at 4000 RPM to give a lump-free solution.

Glass microscope slides were cleaned and degreased by refluxing in tetrahydrofuran solvent. Using vacuum deposition, a 20 nm layer of chromium followed by a 40 nm layer of gold were thermally evaporated onto one side of the glass slides. Cr was used to improve the adhesion of Au to the underlying substrate. This top layer was further rinsed with distilled water.

A 1 cm² gold-coated glass slide was covered with 2 or 3 drops of the polyaniline and spun at 500rpm for 1 minute, 2000 rpm for another minute and 300 rpm for another minute. Films, approximately 100 nm in thickness, were left to dry overnight and were colored yellow/blue in reflected light.

Two or 3 drops of Shipley Microposit Primer were deposited on the Polyaniline film and spun at 3000 rpm for 25-30 seconds. Then Shipley Microposit S1813 (positive

photoresist) was deposited on the top, spun at 3000 rpm for 20-25 seconds, then dried on a hot plate at 80°C for 10 minutes. A 20 W ultraviolet source was used to expose films through the patterning mask for 7 to 10 seconds. Microposit MF 312 developer in half of its original concentration was used as the developer.

Nitric acid was used to etch away the exposed polyaniline. Then the slides were rinsed with distilled water and dried under compressed nitrogen gas.

The remaining unexposed photoresist was stripped by stirring it in the Shipley 1112A Microposit remover, which had been diluted to one-third of the original concentration with water. The schematic diagram of this procedure is shown as Figure 2-1.

Figure 2-1. Schematic diagram of photolithography procedure.

As a result, a polyaniline pattern with a width of 15-20 μm was achieved with a good resolution as shown in Figure 2-2. However, the conductivity of the PANI pattern was not reported. After being etched with nitric acid, it had an undetermined level of conductivity.

Figure 2-2. Patterned polyaniline film on a gold-coating glass substrate. ^[12]

This procedure was used to make a charge flow transistor. A schematic diagram of the device is shown in Figure 2-3. The surface scan across the device is shown in Figure 2-4. As can be seen, the surface profile of the PANI pattern is not even. The pattern properties and the characteristics of the transistor were not reported.

Figure 2-3. Schematic diagram of a charge flow transistor (CFT) device.

Figure 2-4. Surface profile scan across a CFT device. The dashed lines present the PANI patterns.^[12]

2.2 Water Soluble Conducting Polyanilines: Applications in Lithography

Angelopoulos^[13,14] *et al.* developed a class of water-soluble conducting polyanilines, PanAquasTM, which can be patterned through E-beam lithography technology. The synthesis of polyaniline was modified to produce polyaniline derivatives which are water soluble (in the conducting form). The appropriate aniline monomer was complexed to a template, such as a polymeric acid, denoted as polyacid in Figure 2-5. The complex is then oxidatively polymerized by ammonium persulfate to produce a conducting polyaniline/polyacid blend. By controlling the reaction parameters such as temperature, concentration, and stoichiometry, the blend can be made water-soluble. However, these parameters were not reported in this paper.

Twelve percent PanAquasTM was spin-coated onto a silicon oxide wafer. The film was baked at 80°C on a hot plate for 3 minutes, then exposed to a 50 keV Gaussian E-beam, then postbaked at 80°C for 5 minutes. A conducting 1.0 μm pattern was generated, as shown in Figure 2-6. The properties and characteristics of the pattern were not reported.

Figure 2-5. Template synthesis of water-soluble polyaniline. The aniline monomer is complexed to a polyacid, then oxidatively polymerized. ^[13]

Figure 2-6. One μm conducting polyaniline lines in a $0.75\ \mu\text{m}$ thick film patterned by E-beam irradiation. ^[13]

2.3 Deposition of Conducting Polyaniline Patterns with the Scanning Electrochemical Microscope

Junfeng Zhou ^[15] and David Wipf used the Scanning Electrochemical Microscope (SECM) to deposit polyaniline patterns on gold, platinum, and carbon surfaces. The SECM is a scanned-probe microscope designed for making images of a surface immersed in an electrolyte solution. As illustrated in Figure 2-7, the SECM can be used to locally reduce the proton concentration through the reduction of protons and/or water at the SECM tip. A localized deposition of polyaniline features can be made by using the proton concentration sensitivity of aniline oxidation.

Figure 2-7. Illustration of the SECM polyaniline deposition process.

The solution was prepared with aniline (98%, Aldrich), hexaammineruthenium(III) chloride (Stream Chemical) and 18 M Ω distilled-deionized water. Ag/AgCl (3M NaCl) was used as a reference electrode for all experiments. The auxiliary electrode was a Pt wire. Three different tips (100, 10 and 2 μ m diam Pt) and 8 μ m diam carbonfiber electrode were used.

The resolution of polyaniline patterns was determined by the tip size, substrate potential, tip-substrate distance, tip potential, and tip scan speed. Tip size was the primary factor. By controlling these factors, a 3 μ m pattern with conductivity of 0.18 S/cm was produced. Figure 2-8 is a microscope image of PANI patterns made by the SECM method. (Deposition conduction: substrate potential is 600mV, tip potential is -1400mV, tip-substrate distance is about 1 μ m, and the tip scan speed is 0.5 μ m/s)

Figure 2-8. A microscope image of a PANI pattern deposited on a Au substrate using a 10 μ m Pt tip electrode. ^[15]

2.4 Microfabrication of Interdigitated Polyaniline/Polymethylene Patterns on a Gold Surface.

Tao ^[16] *et al* took advantage of the characteristics of self-assembled monolayers (SAMs) and applied the microcontact printing (μ CP) technique to pattern polyaniline and polyethylene patterns on a gold surface. The schematic diagram of the experiment is shown as Figure 2-9.

Figure 2-9. Fabrication of patterned polymethylene-polyaniline film. ^[16]

In the μ CP method, a stamp is prepared by molding a silicon elastomer against a photolithographically or mechanically patterned master. The stamp is then used to transfer a monolayer pattern to the gold substrate. The stamp was inked with alkanethiol ($C_{20}H_{41}SH$), then contacted to a gold substrate.

Tao, et al, used a 1mM solution of thiol ethanol ink solution and made a stamp from a silicon wafer. The substrate was inked by μ CP, then was exposed to diazomethane to grow the polymethylene. The areas coated with the thiol ethanol protected the underlying gold. These polymethylene patterns were insulating and stable under electrochemical and chemical etching conditions. These insulating polymethylene patterns permitted the fabrication of patterns of conducting polyaniline which were intercalated with the polymethylene patterns.

The substrate was placed in a cell containing 0.1 M aniline in 0.85 M H_2SO_4 and 0.25 M $NaHSO_4$ solution, and the potential applied to the substrate was between -0.2 and 0.85 V versus Ag/AgCl. The cycling was terminated at 0.4 V versus Ag/AgCl, so that the film was at its reduced state (emeraldine form). The substrate was then washed with ultrapure water and dried with a slow stream of nitrogen.

Conducting polyaniline patterns with 2 and 3 μ m, width were produced, as shown in Figure 2-10. The dark region represents the polyaniline part, which is conducting. The lighter region represents the polymethylene part, which is non-conducting. Properties of the polyaniline patterns were not reported.

Figure 2-10. A SEM micrograph of polyaniline polymethylene patterns on gold. ^[16]

2.5 Summary of Literature Review

PANI can be patterned in micro dimensions which are conductive by using either photolithography or electrochemical techniques. In the former technique, it is difficult to produce a PANI coating, since the conducting PANI is not processible, due to its poor dissolution in solvents. Research efforts into the photolithography method have focused on either improving the dissolution rate of the base form of nonconductive PANI, or on modifying the conducting PANI to a soluble form. For the electrochemical deposition methods, the drawback is that they are not commercially efficient.

There is no PANI/polymer pattern reported in the literatures at this time. PANI patterns reported were all single component and expected to have poor mechanical properties. The current literature lacks reports on the properties of PANI patterns, such as adhesion, mechanical properties and stability. This information will be important and necessary for further research on the application of PANI.

3.0 EXPERIMENT

3.1 Preparation and Process

The flow chart for the experimental process is shown in Figure 3-1. The details for each step are described in the following sections.

3.1.1 Preparation of Formulation

Formulations containing different amounts of PANI (Versicon, Allied-Signal) and photoresist (OCG-20cs) were prepared by adding a weighted amount of PANI to the photoresist solution. The dispersion of PANI in the formulation was achieved by sonicating the formulation for 30 minutes. All formulations were prepared in a UV-free environment. The composition of each formulation was defined in terms of the weight of PANI to the total weight of the solids in the formulation, as shown in Equation 1. The solids content of the photoresist solution was 33.32 wt % of the total weight. This determination was made by allowing a weighed amount of photoresists to dry to completion for 72 hours, then weighing the remaining solids. With this content, a formulation containing 1 weight unit of PANI and 7 weight unit of photoresist solution then produced a film having a 30 wt % PANI, $[1 / (1 + 7 \times 33.32\%) = 30\%]$.

$$\text{Composition of formulation} \equiv \frac{\text{Wt. of PANI}}{\text{total Wt. of solids in formulation}} \% \quad [\text{Eq-1}]$$

Figure 3-1. Experiment flow chart.

3.1.2 PANI/Novolac Coatings

Film Coatings: Three types of substrates were used in this study: microscope cover glasses, silicon wafers and oxidized silicon wafers. Glass slides were used to develop the process parameters. Silicon wafers were the desired substrates; however, they are conductive and interfered with the conductivity measurements of the PANI/Novolac patterns. Therefore, the silicon wafers were oxidized to grow an electrically insulating SiO₂ thin layer. The presence of this oxide layer was important for the PANI/Novolac pattern conductivity measurement.

Glass substrate: Microscope cover glasses (VWR, 25mm) were cleaned by soaking them in a NaOH/Methanol solution to remove cluster impurities and grease from the surface, then rinsed with D.I. water. Next, they were blow-dried with air and baked in an oven at 145 °C for 15 minutes.

A pure photoresist was coated on the substrates first to improve the adhesion between the PANI/Novolac film and the glass substrate. To produce this coating, seven drops (0.29 ml) of pure photoresist (OCG-20cs) was placed on a glass substrate and spun by a Headway Spinner at 3500 rpm for 40 seconds. This produced a 0.8 μ m thick film. The coated substrates were baked in an oven at 100 °C for 10 minutes.

To produce the PANI/Novolac coating, ten drops (0.42 ml) of PANI/photoresist formulations were then applied onto the pre-coated glass substrate, and the substrate was spun at 2500 rpm for 40 seconds. This produced a non-sticky film on a glass substrate.

The minimum rate for the single-speed coating of PANI/Novolac formulations on glass substrates was found to be 2500 rpm. In addition, two critical spinning rates were

noted. The 300 rpm was the minimum rate for the spinner to spin smoothly. A minimum spinning rate of 600 rpm was required to spread the formulation onto the substrates. With these three critical spinning rates, two other spinning conditions were tried. They are described as follows:

- ① For a 2-stage coating: 600 rpm for 120 seconds, then 2500 rpm for 2 seconds.
- ② For a 3-stage coating: 600 rpm for 5 seconds, 300 rpm for 120 seconds, then 2500 rpm for 2 seconds.

Ideally, the first spinning spread the formulation onto the substrates, and the final spinning process removed the residue around the edges of glass substrates. [The spinning rates were approximate, due to the accuracy of the equipment]

Silicon wafer: Wacker Silicon wafers (<111>, 62mm, n type, P-doping, $\sigma = 0.022 - 0.033$ S/cm) were either used as received or surface oxidized in a 1100 °C furnace for 28 hours. The surface silicon dioxide film was about 0.3 μ m according to the purple color on the oxide. The silicon wafers were dried at 150°C for 12 minutes before applying the PANI/photoresist coating.

Sixty-five drops (2.73 ml) of 30 wt % PANI/Novolac formulation were applied to the silicon wafer, then, the wafer was spun at 600 rpm for 120 seconds, then at 1100 rpm for 2 seconds. Since the chuck of the spinner did not hold the wafers tightly at the high spin rates, (> 1500 rpm), a lower spin rate, 1100 rpm, was used to drive off the formulation residue around the substrate edge.

3.1.3 Patterning Process

Prebake (Softbake): The coatings were dried at 90-100°C for 10 minutes in an oven. This is the recommended treatment for the pure photoresist from the vendor. A prebake condition of 60°C for 24 hours was also used.

Exposure: Apollo transparency film (PP 100C) was used to make the photolithography mask shown in Figure 3-2. The 1mm wide toner patterns on the mask were printed by a laser printer. Four 100W Mercury lamps were used as the UV source for photolithography, and the effective intensity on the substrate was about 200W. For the pure photoresist, one minute of exposure was enough. The minimum exposure time for coatings with more than 25% PANI was about two minutes. The actual time needed was generally between 3 to 3.25 minutes.

Figure 3-2. The patterns on the mask.

Development: The development procedures and developers used varied for different substrates.

Glass substrate: For the PANI/glass coatings, the exposed specimens were vertically dipped into the commercially available OCG 934 3:2 Developer (Tetramethyl ammonium hydroxide, TMAOH). This is the developer normally used for a positive photoresist. During the immersion, the specimens were raised and lowered in the solution. This must be done gently because the coating can be easily lifted off the glass substrate. Every 10 to 15 seconds, the specimens were removed from the developer and rinsed in D.I.-water, then placed back in the developer. This procedure was repeated until the pattern had been generated on the glass substrate.

Some vague patterns could be visually seen on the UV-exposed films even before immersion in the developer. A clear pattern normally appeared after approximately 1.5 minutes in the developer. After another 2(+/-) minutes of immersion the exposed areas on the coatings began to wash away. After approximately 4.5 minutes of total immersion, the coatings began to lift off the substrates.

Silicon wafer: Exposed coatings on silicon wafers were immersed in a 0.15 M NaOH solution in a 250 ml glass beaker. The beaker was placed in an ultrasonic cleaner to assist in the pattern development. The sonication was employed with caution because the temperature of the solution increased and water evaporated during the sonication. This concentrated the NaOH solution. At 15-minute intervals, the specimens were rinsed in D.I water, then placed back to the solution. Development was complete when clear

patterns on the wafers had been generated.

Postbake: Patterns were dabbed lightly with tissue paper to remove the excess liquid, then dried in an oven at 105°C for 10 minutes.

Conductivity Recovery: Since the hydroxide in the developer neutralized the PANI into the nonconductive emeraldine base form, a subsequent acid treatment was used to recover the conductivity of the PANI/Novolac pattern. The conductivity of the 30 wt % PANI patterns on the glass and bare silicon substrates was recovered by exposing them to acid vapors. The substrate was placed upside down on the open end of a small vial (25 ml) which was filled with 5 ml of 2N HCl. The Patterns were approximately 4 cm from the surface of the solution. Both HCl solutions at room temperature and at 38°C were used in this study. The exposure stopped until the PANI/Novolac pattern provided a response to the voltmeter.

3.2 Characterization:

3.2.1 Electrical Properties

A 4-point probe, Keithley Model 177 Microvolt DMM, was used to determine the resistance of the PANI/Novolac coatings. Two electrodes were placed on the coatings with a separation distance of 5 mm. If the measured resistance was less than 201.1 Ohm, which is the limit of the voltmeter, the film was considered to be conducting.

A Fell Resistivity Equipment Model B (Minirodion LTD.) was used to measure the resistivity of the coatings. The conductivity (σ) of a material is related to its resistivity (ρ) as shown in Equation 2.

$$\sigma = \frac{1}{\rho} \quad [\text{Eq-2}]$$

For a rectangular block, the resistance(R , units in ohms) is related to the resistivity as in Equation 3, where, l = the contact to contact separation, w = width, t = thickness, and A = the cross-sectional area of the specimen (Area =thickness $\times$ width).

$$R = \frac{\rho l}{w \times t} = \frac{\rho l}{A} \quad [\text{Eq-3}]$$

In addition, R is related to the applied voltage (V) and the current (I) by $V=R \times I$. The sheet resistivity (R_s , ohms per square) of a material is an often-measured parameter and is defined in Equation 4. In this equation, 4.53 is a correction factor. A 4-point probe, as shown in Figure 3-3, is used to determine the values of V and I .

$$R_s = 4.53 \frac{V}{I} \quad [\text{Eq-4}]$$

This equation is valid only when the thickness of the layer being measured is much less than the spacing between the probes, and when the size of the piece of material being measured is much greater in length and width than the probe spacing.

For a thin film with uniform composition and thickness, the resistivity (ρ) is calculated using Equation 5.

$$\rho = R_s \times \text{thickness (t)} \quad [\text{Eq-5}]$$

A V/I 4-point probe was used to measure the V and I, and σ was calculated using Equation 6.

$$\sigma = \frac{I}{4.53Vt} \quad [\text{Eq-6}]$$

Figure 3-3. The schematic of a 4-point probe.

Since the PANI/photoresist formulation is a 2-phase system, the spin-coated film is expected to be non-homogeneous in the PANI distribution and the conductivity. A systematic method was developed to measure the conductivity of the PANI/Novolac coating. The conductivity of each coating was measured at six locations, using the design shown in Figure 3-4. The average of the six measured values was recorded.

Figure 3-4. The design of the conductivity reference locations on a coating.

3.3.2 Physical Properties

A profilometer (Alpha-step Profiler, Tencor Instruments) was used to measure the thickness of a given film. A scratch was made on the coating down to the surface of the substrate. Then a fine diamond stylus was drawn over the surface of the substrate-coating edge and its vertical motion was measured by a linear variable differential transformer. [The specifications for the surface profilometer indicated that it can measure coating thickness down to 100 angstroms.]

The adhesion of the coating was tested by a tape test. 3M Scotch tape was placed on the coating surface, then pulled off manually. The quality of the coating adhesion was determined by the amount of the coating remaining on the substrate. The coatings with better adhesion were not removed by the tape. The edge definition of the patterns was observed using a Nikon microscope equipped with a camera.

4.0 RESULTS AND DISCUSSION

4.1 Formulations

Twelve formulations containing 0 to 45 wt % PANI were prepared. The compositions are listed in Table 4-1, and the "P-notation" was used to identify the various coatings. For example, a coating containing 30 wt % PANI was labeled P-30. Dispersions with 45 or more wt % PANI could not be obtained with this dispersing procedure. Formulations with more than 20 wt % PANI had many large particles, which could not be eliminated even through 1-2 hours of sonication.

Table 4-1. Summary of the compositions of the formulations and the respective coatings.

Sample	Formulation			Coating	
	PANI	Photoresist		PANI	Novolac Resin
		Solids	Solvent		
P - 0	0.0%	33.3%	66.7%	0%	100%
P-10	3.6%	32.1%	64.3%	10%	90%
P-20	7.7%	30.8%	61.6%	20%	80%
P-25	10.0%	30.0%	60.0%	25%	75%
P-25(conc.)	11.1%	33.4%	55.5%	25%	75%
P-27.5	11.2%	29.6%	59.2%	27.5%	72.5%
P-29	12.0%	29.3%	58.7%	29%	71%
P-30	12.5%	29.2%	58.3%	30%	70%
P-31	13.0%	29.0%	58.0%	31%	69%
P-35	15.2%	28.3%	56.5%	35%	65%
P-40	18.2%	27.3%	54.6%	40%	60%
P-45	21.4%	26.2%	52.4%	45%	55%

4.2 PANI/Novolac Coatings

4.2.1 Spin-coating Method

Films which were coated on 25 mm glass substrates using 2500 rpm did not result in a homogeneous distributions of PANI. "Sea waves" and "radial lines" could be seen visually. The "sea waves" were associated with discontinuities in the PANI distribution, as shown in Figure 4-1. This figure is a photograph of a P-40/glass coating with a magnification of 200X. The white regions represent the photoresist and the black regions represent PANI. The electrical resistance of six reference locations on each coating, produced by various spin rates, was measured by a voltmeter, as shown in Figure 3-4. Two samples were tested for each coating. The average resistance values are listed in Table 4-2. As shown in this table, both the spin rate and PANI content affected the resistance of the coatings. The PANI content appears to be the more critical factor. Coatings with less than 30 wt % PANI were electrically resistant ($>20\text{M } \Omega$) and those with 30 wt % or more were conductive, and the conductivity was relational to the PANI content. For a given formulation, a lower spin rate produced a less resistive coating. It would appear that the high spin rates drove the PANI particles off the substrate.

The distribution of the PANI particles was not homogeneous through the coatings. The non-homogenities could be detected by measuring the resistance. The center region showed less resistance than the edge region. For example, the resistance of P-30 film coated at 2500 rpm was $14\text{M}\Omega$ in the center region (5mm radius), and was $> 20 \text{ M}\Omega$ in the edge region.

Figure 4-1. A photograph (200X) of P-40/glass showing the "sea waves".
(Process: 2500 rpm, 40 seconds)

Table 4-2. Measured resistance of the coatings on glass substrates through single-speed coating methods.
(Resistance, $M\Omega$)

Spin Rate*	Coating							
	P-0	P-10	P-25	P-27.5	P-29**	P-30**	P-35	P-40
2500rpm	NR	NR	NR	NR	17	14	2.5	0.5
3000rpm	NR	NR	NR	NR	NR	17	4.0	1.5
3500rpm	NR	NR	NR	NR	NR	18	10	2.9
4000rpm	NR	NR	NR	NR	NR	19	11.5	3.5
Remarks	NR - no response from the voltmeter; $>20M\Omega$. * 40 seconds coating time. ** The resistance only available in the center region, 5 mm radius.							

4.2.2 Multiple-speed Method

Six coatings, P-27.5 to P-40, were prepared through a 2-stage and a 3-stage speed method. Both multiple-speed coating methods produced coatings with better PANI distribution than the single-method. The "sea wave" and "radial line" characteristics were not observed, but some larger particles and clumps appeared. The coatings made by the multiple-speed methods still did not cover on the glass substrates evenly. With the 2-stage method, there was a 2 mm ring around the edge of the substrate, which was lighter in color and contained less PANI. With the 3-stage method, this ring was about 4mm in width. Figure 4-2 illustrates the coatings produced through both multiple-speed methods.

2-stage coating method 3-stage coating method

Figure 4-2. Coatings produced through two multiple-speed coating methods.

The coatings obtained by the 2-stage method had a good PANI particle distribution. This can be seen in Figure 4-3, which is a 200X magnification photograph of a P-30 film produced by the 2-stage method. The particle distribution was quite good, even though there were some clumps. The average size of the particles was about $5\text{ }\mu\text{m}$, and there were a few large particles, $20\sim 35\text{ }\mu\text{m}$. The coatings obtained by the 3-stage method had fewer but bigger clumps, were wet and difficult to produce reproducibility. This method was not pursued further.

The characteristics of the coatings from the 2-stage and the 3-stage methods are listed in Table 4-3. As can be seen, the 3-stage method produced thicker coatings with less electrical resistance. However, coatings produced by the 2-stage method had better adhesion. These coatings made by the 2-stage method remained partially on the glass substrates after the tape test, while the coatings produced by the 3-stage method were completely lifted off the glass substrates.

In a separate experiment, a P-25 formulation, P-25(conc.), was concentrated by allowing the solvent to evaporate. From the weight loss, it was calculated that the solvent content was reduced from 60% to 55.5%. This concentrate was used to coat substrates by both multiple-speed methods. In both cases, the resulting coatings were electrically resistant, $> 20\text{M}\Omega$. Based on the results, it was determined that the more viscous formulation does not generate conductive coatings.

Considering the conductivity, adhesion, and the coating reproducibility, the 2-stage method was considered the most suitable method to spin-coat the PANI/Novolac coatings and was used in all subsequent experiments.

Figure 4-3. A microscope photograph of a P-30/glass coating. (200X magnification)

Table 4-3. Characteristics of coatings prepared by the two multiple-speed coating methods.

		2-stage method (600 rpm-120s, 2500 rpm-2s.)	3-stage method (600 rpm-5s, 300 rpm-120s, 2500 rpm-2 s.)
P-27.5 To P-40	General Properties	Dried film. Good PANI distribution. Few clumps. Films stayed on substrates longer while immersed in developer.	Wet film. Better PANI distribution (not all the time). Some clumps. Films lifted off in developer easily.
P-27.5	Resistance (Ω)	> 20M	> 20M
	Thickness (μ m)	2.2-3.2	3.2-4.0
	Tape test	Lifted off slightly	Lifted off partially
P-29	Resistance (Ω)	Average: 1240k Range: 970-2340k	Average: 635k Ω Range: 570-1340k
	Thickness (μ m)	3.0-4.2	4.5-5.5
	Tape test	Lifted off partially	Lifted off completely
P-30	Resistance (Ω)	Average.: 1190k Range: 830k - 1800k	Average.: 585k Range.: 450k - 830k
	Thickness (μ m)	3.0-4.2	4.5-5.5
	Tape test	Lifted off partially	Lifted off completely
P-31	Resistance (Ω)	Average.: 970k Range: 690k - 1450k	Average.: 510k Range.: 325k - 810k
	Thickness (μ m)	3.0-4.2	4.5-5.5
	Tape test	Lifted off partially	Lifted off completely
P-35	Resistance (Ω)	Average: 550k Range: 323k- 606k	Average: 240k Range: 240k-130k
	Thickness (μ m)	4.7-6.3	6.5-7.5
	Tape test	Lifted off completely	Lifted off completely
P-40	Resistance (Ω)	Average: 330k Range: 121k-450k	Average: 22k Average: 17k-31k
	Thickness (μ m)	6.2-7.7	10.0-14.0
	Tape test	Lifted off completely	Lifted off completely

4.3 Characteristics of Coatings through a 2-stage Method

Coating Thickness. The thickness of the coatings resulting from the 2-stage method was found to be uneven. It varied along the radius of the substrate and decreased towards the edge. Figure 4-4 shows the profilometer traces for the P-30, P-35, and P-40 coatings in the region 2 mm from the center point (left), and the region 8 to 10 mm from the center point (right). Plotted in Figure 4-5 is the thickness of the P-29, P-30, P-31, P-35, P-40 coatings on glass substrates. The coating thickness was measured every 2 mm from the center to the edge. Each point on the graph is the average thickness for each measured point. The actual measured values for three coatings are listed in Appendix A. Using this plot, the actual thickness of given coatings could not be predicted, but a pattern of thickness distribution in the coatings could be interpreted. As shown in Figure 4-5, the thickness variation along the radius can be divided into two regions; the center region, with an approximately 5mm radius, and the edge region, approximately 7.5 to 10 mm away from the center. The formulations with a higher PANI content produced a thicker coating. The thickness produced by the 2-stage method was 6.2 to 7.7 μm for P-40, 5.0 to 6.5 μm for P-35 coating, 3.0 to 4.2 μm for P-29, P-30 and P31 coatings. The 2mm ring around the edge was not evaluated and the thickness of the photoresist layer, approximately 0.8 μm , was subtracted. The thickness variation is viewed as reasonable and strongly dependent on the spinning speed. It would appear that the Headway spinner did not have good spin rate control and this contributed to the thickness variations. In addition, the two-phase nature of the formulation affected the reproducibility of the process. Development of a better coating method, or finding a way to reduce the PANI

particle size would help improve the coating quality for future experiments.

Figure 4-4. Profilometer traces for three coatings. (2-stage method)

Figure 4-5. Thickness distribution of P-27.5, P-29, P-30, P-31 and P-40 coatings on glass substrates. (2-stage method)

Surface Roughness. From a profilometer trace across a coating surface, the surface roughness could be estimated. The roughness was estimated by the displacement of the stylus between the "valleys" and the "peaks" in the trace. Sharp spikes were not included in this estimation, because they represented "over shots" caused by large particles. The profilometer trace for the P-30 coating is shown in Figure 4-6. In this profilometer trace, the flat line at the left indicates the surface of the glass substrate, and the step is the edge of the coating and the substrate. The scanned distance in the trace is approximate 3 mm. The roughness of this coating surface was approximately $\pm 1.5 \mu\text{m}$. This was significant since the coating was 3-4 μm thick. The other coatings, P-29, P-30, P-31, P-35, and P-40, showed the same surface roughness. In addition, the roughness was consistent throughout the surface of the coatings. This can be seen in Figure 4-4. For comparison, a profilometer trace of an un-coated glass substrate surface is shown in Figure 4-7. As shown, the glass surface is very smooth and should therefore not be a contributing factor in the coating surface roughness.

Figure 4-6. The profilometer trace for a P-30 coating. (2-stage method)

Figure 4-7. The profilometer trace for a glass substrate surface.

Conductivity. The conductivity values of the coatings are the averages of several measurements. The conductivity value for the center region is the average of the measurements at two reference locations, and the conductivity of the edge region is the average of the measurements at four reference locations. The variation in conductivity was due in part to the condition of the equipment. The conductivity and thickness of P-29, P-30, P-31, P-35 and P-40 coatings are listed in Table 4-4. The P-29, P-30, P-31 coatings showed a similar conductivity, 0.0012 ± 0.00002 S/cm in the center region, and 0.0009 ± 0.00012 S/cm in the edge region. These low values reflected a small number of connective paths and the poor PANI dispersion in coatings. With the P-35 coating, the conductivity dramatically increased to 0.025 ± 0.0017 S/cm (center region) and to 0.014 ± 0.0028 S/cm (edge region). For the P-40 coatings, the conductivity was 0.027 ± 0.0026 S/cm (center region), and 0.016 ± 0.003 S/cm (edge region). For a given coating, the center region proved to be thicker and had a higher conductivity than the edge region. The conductivity and the thickness of the coating increased with the increased PANI content under the same coating method.

For comparison purposes, a PANI-only coating and a PANI pellet were prepared. Ten drops (0.42 ml) of a 30 wt % PANI/Ethyl 3-Ethoxypropionate (solvent for the OCG-20 photoresist) formulation was placed on a glass substrate, then spun at 300 rpm for three seconds to produce the coating. The coating was allowed to air dry at room temperature. This deposition was a continuous film, which was so fragile that it could be wiped off, as well as having poor adhesion. The resulting $30 \pm 2 \mu\text{m}$ thick PANI deposition had a conductivity of 0.88 ± 0.053 S/cm. Alternatively, a PANI pellet (0.065g

0.51 mm in thickness, and 12.2 mm in diameter) was prepared by compression under 4570 psi using a Lincoln Hydraulic Press. The conductivity of this PANI pellet was about 2.5 ± 0.064 S/cm. The results showed that the conductivity of the P-30 composition films was 730 times lower than a single component PANI coating and 2100 times less than the bulk PANI. For comparison, the conductivity of this commercial PANI is reported to be 2 to 4 S/cm by the vendor, and the conductivity of the PANI pattern has been reported to be 0.18 S/cm by Zhou^[15].

Table 4-4. The conductivity and thickness of P-29, P-30, P-31, P-35, P-40 coatings through the 2-stage coating method.

	Region	Average Thickness (μm)	Conductivity (S/cm)
P-27.5	Center	3.20 ± 0.45	0
	Edge	2.20 ± 0.25	0
P-29	Center	3.67 ± 0.03	0.0012 ± 0.00002
	Edge	2.87 ± 0.11	0.0009 ± 0.00012
P-30	Center	3.67 ± 0.03	0.0012 ± 0.00002
	Edge	2.87 ± 0.11	0.0009 ± 0.00012
P-31	Center	3.67 ± 0.03	0.0012 ± 0.00002
	Edge	2.87 ± 0.11	0.0009 ± 0.00012
P-35	Center	5.70 ± 0.00	0.025 ± 0.0017
	Edge	5.20 ± 0.50	0.014 ± 0.0028
P-40	Center	7.60 ± 0.27	0.027 ± 0.0026
	Edge	7.06 ± 0.44	0.016 ± 0.003
Pure PANI Coating		30.0 ± 2.00	0.88 ± 0.053
PANI Pellet		510	2.50 ± 0.064

4.4 Patterning Process

4.4.1 Prebaking

P-30 coatings were baked at either 100-115°C for 10-12 minutes or 60°C for 24 hours in an oven. No visual difference appeared on the pattern, however, the prebake conditions did effect the development process. This is discussed below. Based on these results, all the other coatings were prebaked at 100-115°C for 10-12 minutes.

4.4.2 Exposure and Development

All coatings were exposed to UV light. Coatings with less than 25 wt % PANI were easily patterned and usually required less than 2 minutes of exposure. P-25 and P-30 coatings required 3 - 3.25 minutes of exposure. With the P-40 coating, however, even 4 minutes of exposure were not long enough to produce a pattern, and the required exposure time was not established. In general, coatings with less PANI content had better photoresponse, and required shorter exposure times. The color of the exposed areas changed on the coatings which had more than 25 wt % PANI. The exposed area became a darker green which was enhanced with increased exposure time. These results are summarized in Table 4-5 and plotted in Figure 4-9. These coatings were prepared by the 2-stage coating method, and prebaked at 100°C for 100 minutes. TMAOH was used as developer.

Coatings with 25 or less wt % PANI produced patterns with clear edges and good adhesion to the glass substrate. The edges were straight and most exposed areas were removed. No PANI was removed from the protected area along the edge. P-30, P-35 and

P-40 coatings also produced patterns, however, the edges were not as well defined. Both exposed and unexposed regions of the coatings usually lifted off the glass substrates when immersed in the TMAOH developer solution, even before the patterns were fully developed. For example, the P-30 coatings patterns lifted off in the TMAOH developer solution at approximately 4 minutes. In general, the qualities of the developed patterns became worse with increasing amounts of PANI. These results are summarized in Table 4-5.

Table 4-5. Summary of photoresponses of the PANI/Novolac coatings.
(Process: 2-stage method, prebake-100°C for 10 minutes, TMAOH)

	P-0	P-10	P-25	P-27.5	P-30	P-35	P-40
Photoresponse	Excellent		Good				Poor
Exposure Time	< 2 minutes			3 - 3.5 minutes			> 4 minutes
Adhesion	Excellent		Good	Lifted off before fully developed			
Particle Size	Even	→	→	→	→	→	→ Uneven
Edge Definition	Sharp	→	→	→	→	→	→ Rough

For comparison, the edge of a photoresist pattern (containing no PANI) and the edge of the pattern on the mask is shown in the 200X magnified photograph in Figure 4-8 (a, b). In Figure 4-8 (a), the darker region on the right is a photoresist pattern and the lighter region on the left is the glass substrate. The photoresist pattern is approximately 2 μ m

thick and very smooth. Any variation in the thickness of this coating was too small to be detected by the profilometer, however, there is a $25\text{ }\mu\text{m}$ wide step along the edge of the pattern. The edge of the pattern is very straight, even though the edge on the mask is rough, as shown in Figure 4-8 (b). As can be seen, there is a $\pm 12.5\text{ }\mu\text{m}$ variation in the straight line along the edge in the pattern on the mask. This photoresist coating had good adhesion and remained on the substrate during the development.

The effect of the prebake conditions on the P-30 coatings was observed during development. A lower temperature-longer time prebake lengthened the development time, since the dissolution rate was dependent on the amount of solvent remaining in the final film. A comparison of the effect of the two different prebake conditions on a P-30 coating is shown in Table 4-6. These coatings were prepared using the 2-stage coating method, exposed to UV light for 3 minutes, and developed with TMAOH.

Table 4-6. Effect of the prebake conditions on P-30 coatings.
(Process: 2-stage method, 3 minutes of exposure, TMAOH developer)

Prebake	Time		Pattern quality
	Dissolution of exposed area	Complete lift-off	
100-115°C/ 10-12 min	2.5 minutes	4 minutes	OK
60°C/ 24 hours	3.5 minutes	4.5 minutes	N/A

After exposure and development, all coatings were dried at 115°C for 10 minutes to harden the PANI/Novolac patterns. This postbake condition did not appear to have any

significant effect on the pattern properties. All remaining water had to be removed, otherwise the patterns with more than 30 wt % PANI content curled up and cracked during postbaking. There was no further investigation of the postbake in this study.

Figure 4-9 shows the results from Table 4-4 and Table 4-5. From this figure, it can be determined that coatings in the composition of 30-35 wt % PANI/Novolac provide the best combination of conductivity and photoresponse.

Figure 4-8. Photographs (200X magnification) of (a) the edge of the photoresist pattern, and (b) the edge of the laser-printer print used as the exposure mask.

Figure 4-9. Conductivity and photoreponse of the PANI/Novolac coatings. (2-stage method)

4.4.3 Conductivity Recovery

The conductivity of the PANI/Novolac coatings was lost during the development process, since the hydroxide neutralized the PANI into the non-conductive emeraldine base form. Therefore, the P-30 patterns were exposed to HCl vapor in an attempt to recover the conductivity. This was expected to occur when the iminic nitrogens on PANI became protonated in the acid solution. It took 75 hours of exposure to enhance the conductivity. The center region of this coating, which had a conductivity of 0.0015 ± 0.00017 S/cm before development, and no conductivity after development, showed a recovery in conductivity of 0.001 ± 0.000006 S/cm. The conductivity of the P-30 pattern recovered up to 69% of the conductivity of the P-30 coating. For the conductivity of the edge region, which was $\sigma = 0.0083 \pm 0.00034$ S/cm before development and lost during the development, there was a recovered conductivity of 0.00005 ± 0.00001 S/cm after the HCl treatment, which corresponded to a 6% conductivity recovery. These results are listed in Table 4-7. The incomplete conductivity recovery may have been due to the loss of PANI particles from the pattern and, consequently, the reduction in the number of connective paths in the pattern. The loss of PANI was evident in the decreased thickness of the pattern. With the loss of PANI from these patterns, there were fewer particles and, correspondingly, fewer number of connective paths. However, the recovered conductivity was still low compared to the conductivity of a $30 \mu\text{m}$ PANI-only coating, which was shown to be 0.88 ± 0.053 S/cm.

Table 4-7. The conductivity change of the P-30 pattern after an acid treatment.

		Center Region	Edge Region
Before Development	Thickness (μm)	3.7 ± 1.5	3.0 ± 1.5
	Conductivity (S/cm)	0.0015 ± 0.00017	0.00083 ± 0.00034
After Development	Thickness (μm)	3.2 ± 1.5	2.2 ± 1.5
	Conductivity (S/cm)	0	0
After Acid Treatment	Thickness (μm)	3.2 ± 1.5	2.2 ± 1.5
	Conductivity (S/cm)	0.001 ± 0.000006	0.00005 ± 0.00001
Percent Recovery		69%	6%

4.5 One mm 30 wt % PANI/Novolac Lines

Based on the results in previous sections, the 30 wt % PANI formulation was selected for the following study. This formulation was applied to three different substrates and the process for generating the patterns was further developed. The patterning process and pattern properties for each type are discussed, and only the center region of the coating was characterized.

4.5.1 30 wt % PANI/Novolac Lines on A Glass Substrates

The steps in the patterning process for 1mm P-30 lines are listed in Table 4-8. The patterns were generated using the mask shown in Figure 3-2. Figure 4-10 is a photograph of the 1mm P-30 lines on a glass substrate. As shown, the patterns were not developed completely, since liquid development was stopped early to avoid lift-off of the patterns. The edge of the resulting 1mm P-30 lines is shown in Figure 4-11, which is a microscope photograph using 50X magnification. As viewed, the edge is not clean, and some PANI remained into the exposed region. The distance from the high and low points along the two edges was 100 - 140 μ m. This corresponded to a resolution of approximately 220 μ m. There was also a spur in the exposed PANI coating along the edge. This spur is shown in the 200X magnified photograph in Figure 4-12. In this photograph, the left side is the exposed region, the right side is the unexposed region. The rough pattern edge resulted from poor development. This may be improved by adjusting the prebake conditions and the concentration of the developer.

The biggest issue regarding the patterns on the glass substrates was the adhesion

problem. The generated pattern lifted off completely from the substrates with 3M Scotch tape. In general, these patterns lifted off the substrates if the immersion time in the TMAOH developer was longer than 4.5 minutes. To prevent this, the coatings were removed from the developer solution before the patterns were fully generated. Consequently, the edge of the resulting pattern was affected.

Table 4-8. Process for 1mm 30wt% PANI/Novolac lines on a glass substrate.

Formulation	P-30 (12.50 wt % PANI with 87.50 wt % OCG 20 Photoresist) Sonication for 30 minutes
Film coating	10 drops (0.42 ml) of formulation spun at 600 rpm for 120 seconds, then 2500 rpm for 2 seconds
Prebake	105°C for 10 minutes
Exposure	3 minutes
Development	OCG 934 3:2 Developer (Tetramethyl ammonium hydroxide, TMAOH) and rinsed by D.I. water
Postbake	105°C for 10 minutes
Acid Treatment	Exposed to acid vapor for 75 hours

Figure 4-10. A photograph of the P-30/glass patterns.

Figure 4-11. A photograph of the 1mm P-30 line on a glass substrate.
(50X magnification)

Figure 4-12. A photograph of the 1mm 30 wt % PANI/Novolac line on a glass substrate. (200X magnification)

Figure 4-13 (a) shows a profilometer trace of a 1mm P-30/glass line patterned in the center region of the glass substrate. The thickness of the pattern was about $3.2 \pm 1.5 \mu\text{m}$. The pattern was thinner than the coating before development. Figure 4-13 (b) is another profilometer trace for the same pattern, which reveals the roughness of the pattern surface. Comparing Figures 4-7 and 4-13 (b) shows that the roughness for a P-30 coating and a P-30 pattern were similar. The exposure and development procedures did not affect the surface roughness, even though they reduced the thickness of patterns. This may have been because the roughness of the pattern is related to the PANI particle sizes and distribution, which is not effected by the development process. For comparison, the trace for the patterned photoresist line is shown in Figure 4-13 (c). As shown, without PANI particles the pattern had a smooth surface.

The properties of a P-30 coating and its 1mm patterned line are summarized in Table 4-9.

Table 4-9. The properties of 1mm P-30 line on a glass substrate.

	Coatings	Patterns
Thickness(μm)	3.6 ± 1.5	3.2 ± 1.5
Conductivity (S/cm); Center Region	0.0015 ± 0.00017	0.001 ± 0.000006
Tape Test	Partially lifted off the substrate	Completely lifted off the substrate
Edge Definition	N/A	Not good; blurred regions along both edges. Some PANI particles in exposed region; $100\text{-}120 \mu\text{m}$.

(a)

(b)

(c)

Figure 4-13. Profilometer traces for (a) a 1mm P-30 line, (b) a P-30 line, and (c) a 1mm pure photoresist line, on glass substrate.

4.5.2 30 wt % PANI/Novolac Lines on Bare Silicon Wafers

The patterning process for 1mm 30 wt % PANI/Novolac lines on a silicon wafer was based on the process used on the glass substrate listed in Table 4-10. The P-30 coating produced on the silicon wafer was inferior to the one produced on the glass substrate, especially in the edge region. Some "sea waves" could be seen, so this region was not evaluated in this study. However, the coating adhesion to the silicon wafer was much better than to the glass substrate. The coating survived the tape test. Due to the better adhesion, it took 24 hours immersion in TMAOH to develop the P-30/Si pattern. A stronger developer (0.15N NaOH) and sonication were used to generate the patterns. Even with this process, it still took 3 hours to generate clear PANI/Novolac lines on a silicon wafer. Figure 4-14 is a photograph of the 1mm PANI/Novolac lines on a bare silicon wafer. The top half was protected with a tape during the patterning procedure, and the bottom half was patterned with 1mm lines. The edges of the pattern produced on the wafer were more even than those on the glass substrate. PANI/Novolac residue did remain in the exposed areas. This is shown in Figure 4-15. In Figure 4-15, the dark region is PANI/Novolac, and the lighter region is silicon. Figure 4-16 is a photograph using 200X magnification of the right side of Figure 4-15. It shows the edge to be very smooth. The variation along the edge was approximately $45\text{ }\mu\text{m}$. It was not possible to measure the conductivity of the coating and patterns with the 4-point probe, because the silicon substrate was also conductive. The resistance (5mm spacing) of the coating as measured by the voltmeter was approximately $1100\text{k}\Omega$.

Figure 4-17 (a) is the profilometer trace of the P-30 coating on the silicon wafer,

which indicates a coating thickness of $4 \pm 1.5 \mu\text{m}$. However, after the exposure and development processes, the thickness of the lines was reduced to $2.5 \pm 1.5 \mu\text{m}$. The surface trace for the P-30 line on the bare silicon wafer is shown in Figures 4-17 (b). This profilometer trace shows the thickness of the P-30 line and shows that some of the PANI particles remain in the exposed region. Figure 4-17 (c) is a profilometer trace for the bare silicon wafer surface. The surface of the substrate is shown to be quite smooth in comparison to the roughness of the coating. This definitely affects the coating adhesion. Table 4-11 summarizes the properties of 1mm P-30/Si line.

Table 4-10. Process for 1mm P-30/Si lines.

Formulation	P-30 (12.5 wt % PANI with 87.5 wt % OCG 20 Photoresist) Sonication for 30 minutes
Film coating	65 drops (2.73 ml) of formulation spun at 600 rpm for 120 seconds, then 2500 rpm for 2 seconds
Prebake	105°C for 10 minutes
Expose	Exposed for 3 minutes
Development	Immersed in 0.15 N NaOH solution with sonication and rinsed by D.I. water
Postbake	105°C 10 minutes
Acid Treatment	Exposed to HCl vapor for 125 hours

Table 4-11. Properties of 1mm P-30/Si line.

	Coatings	Patterns
Thickness(μ m)	4 ± 1.5	2.5 ± 1.5
Conductivity (S/cm); Center Region	0.0021 ± 0.0002	N/A
Tape Test	Did not lift off	Did not lift off
Edge Definition	N/A	Straight Edge. Some PANI in the exposed region.

Figure 4-14. A photograph of 1mm PANI/Novolac lines on a bare silicon wafer.
(Mask shown in Figure 3-2)

Figure 4-15. A 1mm P-30 line on a silicon wafer. (50X magnification)

Figure 4-16. The edge of a 1mm P-30 line on a silicon wafer. (200X magnification)

(a)

(b)

(c)

Figure 4-17. The profilometer traces for (a) a P-30/Si coating, (b) a 1mm P-30/Si line surface, and (c) a bare silicon wafer surface.

4.5.3 30 wt % PANI/Novolac Lines on Oxidized Silicon Wafers

Since the conductivity of the silicon wafer affected the conductivity measurements of the coatings and the patterns, a non-conducting surface oxidized silicon wafer was used to complete the pattern study on the silicon substrate. The oxidation treatment made the silicon surface rougher. This can be seen in the profilometer trace for the surface of the oxidized silicon wafer shown in Figure 4-18. The comparison is shown in Figures 4-17 (c) and 4-18. The surface roughness of the substrate was expected to improve the coating adhesion. The patterning and development processes for 1mm P-30 lines on an oxidized silicon wafer were the same as with the bare silicon wafer (See Table 4-10), and the resulting coating and pattern characteristics on the oxidized silicon substrate were identical to those on the silicon wafer. (See Table 4-11).

Table 4-12 lists the conductivity and thickness values of the P-30 coating and its patterned lines on a silicon dioxide substrate. The conductivity was measured at five designated locations, approximately 10 mm away from the center of the wafer. The P-30 coating on this silicon wafer had a conductivity of 0.0021 S/cm, which was higher than the conductivity of the same coating on the glass substrate, 0.0015 S /cm. Table 4-13 compares the conductivity of the P-30 coatings and 1 mm P-30 lines on a glass substrate and an oxidized silicon wafer. As shown, the conductivity of the P-30 coating and pattern was related to their thickness, where the thicker region the higher the conductivity. This was the case even though the thickness was taken into account in the calculation of the conductivity. The $4 \pm 1.5 \mu\text{m}$ thick coating had a conductivity of $0.0021 \pm 0.0002 \text{ S/cm}$, and the $3.6 \pm 1.5 \mu\text{m}$ thick coating had a conductivity of $0.0015 \pm 0.00017 \text{ S/cm}$. The

$3.2 \pm 1.5 \mu\text{m}$ thick pattern had a conductivity of $0.00105 \pm 0.000006 \text{ S/cm}$, and the $2.5 \pm 1.5 \mu\text{m}$ pattern had a conductivity of $0.00076 \pm 0.0001 \text{ S/cm}$.

Figure 4-18. A Profilometer trace for an oxidized silicon wafer surface.

Table 4-12. The conductivity of P-30 coatings and patterns on an oxidized silicon wafer.

	V(volt)	I (μ A)	ρ (cm/S)	σ (S/cm)
Coating (center region; 4 μ m thick)	1.981	6.338	566.357	0.0018
	2.397	9.635	450.790	0.0022
	1.419	4.512	569.864	0.0018
	2.218	9.454	425.113	0.0024
	1.728	7.450	420.287	0.0024
	Average 0.0021 $\pm$ 0.0002			
Pattern (after acid treatment; center region; 2.5 μ m)	2.010	1.292	1761.861	0.00057
	1.870	1.510	1402.500	0.00071
	0.039	0.0385	1140.140	0.00088
	0.600	0.5360	1267.724	0.00079
	0.775	0.7600	1154.852	0.00087
	Average 0.00076 $\pm$ 0.0001			
Conductivity Recovery Percentage				36.19%

Table 4-13. A comparison of P-30 coatings and 1 mm P-30 lines on a glass substrate and an oxidized silicon wafer. (center region)

		Glass substrate	Silicon Dioxide Wafer
Coating	Thickness (μ m)	3.6 $\pm$ 1.5	4.0 $\pm$ 1.5
	Conductivity (S/cm)	0.0015 $\pm$ 0.00017	0.0021 $\pm$ 0.0002
1 mm Line (after acid treatment)	Thickness (μ m)	3.2 $\pm$ 1.5	2.5 $\pm$ 1.5
	Conductivity (S/cm)	0.00105 $\pm$ 0.000006	0.00076 $\pm$ 0.0001

4.5.4 Comparison with Literature

Four different patterning methods for PANI have been reported in the literature. Bartolomeo used a soluble emeraldine base PANI and UV light photolithography to produce a pattern on gold ^[12]. The resulting pattern showed a huge variation in thickness. Angelopoulus used a water-soluble conducting PANI and E-beam lithography technology to produce patterns on a silicon oxide wafer ^[13,14]. Zhou used a solution of soluble aniline monomer and an electron beam Scanning Electrochemical Microscope to deposit a PANI pattern on gold, platinum, and carbon ^[15]. Tao used a solution of aniline and the electropolymerization method to produce conducting PANI patterns on gold ^[16]. All four methods produced single-component PANI patterns in micro dimensions. However, the conductivity of PANI patterns was provided only in Tao's report. The authors reported conductivity of 0.18 S/cm which was 240 times higher than the value (0.00076 s/cm) for the pattern on the oxidized silicon wafer from this study. The high conductivity value reported by Tao was measured on a gold substrate, and the conductivity of the gold may have contributed to the measured value.

None of the reports described the adhesion of the PANI to substrates. In this study, it was found that the adhesion of the PANI/Novolac patterns depended on the surface roughness of the substrates, and the adhesion of the coatings to the oxidized silicon wafers was better than to the glass substrates. These results suggest that the patterns produced by photolithography on the gold substrates may be poorly adhered. The hardness and mechanical integrity of the PANI patterns was also not reported. In this study, quantitative measurements were not made, however, these PANI/Novolac patterns

were strong enough to resist touching and wiping.

5.0 CONCLUSION AND FUTURE WORK

The results of this study showed that the PANI particles can be processed in a dispersion form and patterned by UV light. A PANI/Novolac formulation could be processed as a photoreactive coating through spin-coating, and used to produce conducting patterns using photolithography. Formulations with 30 - 35 wt % were shown to have the best combination of conductivity and photoresponse. In this range, the conductivity of the coatings was approximately 0.0012 - 0.025 S/cm. The conductivity of a coating increased with the increasing PANI content and with the coating thickness. The electrical properties and thickness of the coatings were strongly affected by the spin coating conditions.

The coatings produced through the 2-stage coating method were approximately 3-4 μm thick. With this spin-coating method, the resulting coating thickness was uneven, and the center regions were always thicker than the edge regions. The coating surfaces were rough, and the variation between the high and low points was approximately $\pm 1.5 \mu\text{m}$. The PANI particle size and distribution affected the surface roughness of the coatings.

The adhesion of the coatings was correlated to the surface roughness of the substrates. A rougher surface provided better adhesion. The relative surface roughness of the three substrates used were $\text{SiO}_2 > \text{Si} > \text{glass}$. If the prebake and development conditions were modified, it might improve the adhesion. The PANI particles also affected the roughness of the pattern edge. Although the pattern edge was straight, a

variation of 50 μm was observed along the edge of PANI/Novolac patterns on the oxidized silicon wafer.

PANI with semiconductor-like conductivity, which can be processed into desired physical configurations, may find many potential applications. For future work, the following is recommended to improve the PANI/Novolac patterns:

1. Use oxidized silicon wafers to maintain good adhesion, or any other enhancement, e.g. primer, to improve the adhesion.
2. Filter the PANI powder to remove particles greater than 4-6 μm diameter, to provide a better formulation and improve the uniformity of the coating.
3. Modify the spin coating to produce a coating with better homogenities in thickness and even PANI particle distribution.
4. Modify the prebake conditions. A longer baking time was found to harden the coating more and improve the coating adhesion to the substrate.
5. Lengthen the exposure time, since PANI can absorb UV light and block UV light to the underlying photoresist. A longer exposure time may be needed as the PANI content increases.
6. Modify development conditions. A stronger developer, or a longer immersion time could improve the pattern edge definition, but would increase the chance of lift-off of the coating.
7. Expose the patterns to the HCl gas instead of the HCl solution to recover the conductivity.
8. Analyse the PANI particle count in the developed patterns.

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Appendix A

The thickness of P-27.5, P-29, P-30, P-31, P-35, and P-40 coatings through the 2-stage method. (Unit: μm)

Location		10 to 12	8 to 10	6 to 8	4 to 6	2 to 4	0 to 2	center
		-10 to -12	-8 to -10	-6 to -4	-4 to -2	-2 to -4	0 to -2	center
P-27.5	#1	1.45	2.2	2.2	2.2	2.95	3.45	3.5
	#2	1.45	2.2	2.2	2.45	3.2	3.45	3.7
	#3	1.7	2.2	2.45	2.7	3.45	3.45	3.95
	Avg.	1.53	2.20	2.28	2.45	3.20	3.45	3.72
	Represent thickness	2.28			3.31			
P-29	#1	1.95	2.95	2.95	3.45	3.7	3.95	4.2
	#2	1.45	2.7	2.95	3.2	3.45	3.7	3.95
	#3	1.7	2.7	2.95	3.2	3.45	3.7	4.2
	Avg.	1.70	2.78	2.95	3.28	3.53	3.78	4.12
	Represent thickness	2.95			3.74			
P-30	#1	1.45	2.95	2.95	2.95	3.45	3.7	4.2
	#2	1.45	2.95	3.2	3.45	3.45	3.95	4.2
	#3	1.95	2.95	3.2	3.2	3.45	3.95	4.45
	Avg.	1.62	2.95	3.12	3.20	3.45	3.87	4.28
	Represent thickness	3.07			3.77			
P-31	#1	1.7	3.2	3.2	3.45	3.45	3.95	4.45
	#2	1.95	2.95	3.2	3.3	3.45	3.7	4.7
	#3	1.95	3.2	3.2	3.2	3.95	3.95	4.45
	Avg.	1.87	3.12	3.20	3.32	3.62	3.87	4.53
	Represent thickness	3.19			3.91			
P-35	#1	2.7	4.7	5.2	5.2	5.45	5.45	6.45
	#2	2.95	5.2	5.2	5.2	5.7	5.95	6.7
	#3	2.95	4.95	5.45	5.45	5.45	5.7	6.45
	Avg.	2.87	4.95	5.28	5.28	5.53	5.70	6.53
	Represent thickness	5.15			5.83			
P-40	#1	4.2	6.2	6.7	6.95	7.45	7.7	7.95
	#2	3.95	6.2	6.95	7.2	7.2	7.7	7.7
	#3	4.2	6.45	6.95	7.2	7.2	7.7	7.7
	Avg.	4.12	6.28	6.87	7.12	7.28	7.70	7.78
	Represent thickness	6.68			7.52			

Appendix B

The resistance of P-29, P-30, P-35, P40 coatings through single speed coating methods.
(Process: 40 seconds) (Unit: $M\Omega$)

Spin rate	Region	P-29	P-30	P-31	P-40
2500 rpm	center 1	18.5	11.9	0.31	0.13
	center2	16.5	16.1	0.45	0.21
	edge 1	>20	>20	3.4	0.67
	edge 2	>20	>20	4.2	0.52
	edge 3	>20	>20	3.6	0.86
	edge 4	>20	>20	3.2	0.57
	average	17 ± 0.5	14 ± 2.1	2.5 ± 1.4	0.5 ± 0.2
3000 rpm	center 1	>20	18.3	0.46	0.34
	center2	>20	16.7	0.67	0.42
	edge 1	>20	>20	4.3	2.7
	edge 2	>20	>20	5.7	1.7
	edge 3	>20	>20	6.3	1.5
	edge 4	>20	>20	4.9	2.1
	average	>20	17 ± 1.3	3.7 ± 2.1	1.5 ± 1.0
3500 rpm	center 1	>20	17.2	3.3	1.8
	center2	>20	18.8	3.1	1.4
	edge 1	>20	>20	11.8	4.5
	edge 2	>20	>20	15.1	3.2
	edge 3	>20	>20	12.4	3.9
	edge 4	>20	>20	14.2	2.3
	average	>20	18 ± 0.8	10 ± 4.5	2.9 ± 0.8
4000 rpm	center 1	>20	19.5	5.3	1.6
	center2	>20	18.5	6.4	1.5
	edge 1	>20	>20	11.7	3.3
	edge 2	>20	>20	13.8	4.7
	edge 3	>20	>20	15.3	4.2
	edge 4	>20	>20	16.2	5.4
	average	>20	19 ± 0.5	11.5 ± 3.7	3.5 ± 1.3

Appendix C

The conductivity of three P-30 coatings measured by a 4-point probe.
(Process: 2-stage coating method)

	Region	V(volt)	I (μ A)	Rs	Thickness (μ m)	ρ (cm/S)	σ (S/cm)
#1	center 1	0.792	2.1980E-06	1.632E+06	3.7	603.9	0.001656
	center 2	0.193	4.2400E-07	2.062E+06	3.7	762.9	0.001311
	Center, Average: 0.001483 $\pm$ 0.00017						
	edge 1	1.543	1.470E-06	4.755E+06	2.7	1283.839	0.000779
	edge 2	0.820	8.400E-07	4.422E+06	2.7	1193.979	0.000838
	edge 3	1.280	1.340E-06	4.327E+06	2.7	1168.334	0.000856
	edge 4	2.120	2.190E-06	4.385E+06	2.7	1184.005	0.000845
	Edge, Average: 0.000829 $\pm$ 0.000034						
#2	center 1	2.345	3.578E-06	2.969E+06	3.7	1098.506	0.000910
	center 2	1.360	2.230E-06	2.763E+06	3.7	1022.196	0.000978
	Center, Average: 0.000944 $\pm$ 0.00034						
	edge 1	1.348	1.8000E-06	3.392E+06	2.95	1001	0.000999
	edge 2	2.650	3.7600E-06	3.193E+06	2.95	941.8	0.001062
	edge 3	3.456	4.5780E-06	3.420E+06	2.95	1009	0.000991
	edge 4	2.659	4.2300E-06	2.848E+06	2.95	840	0.001190
	Edge, Average: 0.001061 $\pm$ 0.000066						
#3	center 1	2.753	6.129E-06	2.035E+06	3.7	763.038	0.001346
	center 2	1.378	2.820E-06	2.341E+06	3.7	830.098	0.001171
	Center, Average: 0.001258 $\pm$ 0.000088						
	edge 1	3.057	4.990E-06	2.775E+06	2.95	818.601	0.001222
	edge 2	2.340	2.560E-06	4.141E+06	2.95	1221.507	0.000819
	edge 3	1.450	1.754E-06	3.745E+06	2.95	1104.736	0.000905
	edge 4	0.453	5.140E-07	3.992E+06	2.95	1177.756	0.000849
	Edge, Average: 0.000949 $\pm$ 0.000137						
Remarks		The reference locations were shown in Figure 3-3.					

The conductivity of three P-35 coatings measured by a 4-point probe.
(Process: 2-stage coating method)

	Region	V(volt)	I (μ A)	Rs	Thickness (μ m)	ρ (cm/S)	σ (S/cm)
#1	center 1	1.210	83.220	65865.177	5.70	37.543	0.0266
	center 2	0.710	50.230	64031.455	5.70	36.498	0.0274
	Center, Average: 0.0270 ± 0.0004						
	edge 1	1.850	78.900	106216.73	5.50	58.419	0.0171
	edge 2	3.770	97.500	175160.00	5.50	96.338	0.0104
	edge 3	2.520	92.500	123411.89	5.50	67.877	0.0147
	edge 4	1.920	73.800	117853.66	5.50	64.820	0.0154
	Edge, Average: 0.0144 ± 0.004						
#2	center 1	1.340	75.300	80613.546	5.70	45.950	0.0218
	center 2	1.780	105.600	76357.955	5.70	43.524	0.0230
	Center, Average: 0.0224 ± 0.0006						
	edge 1	3.001	92.983	146204.47	4.70	68.716	0.0146
	edge 2	2.320	100.320	104760.77	4.70	49.238	0.0203
	edge 3	4.102	137.456	135185.51	4.70	63.537	0.0157
	edge 4	2.470	108.350	103268.11	4.70	48.536	0.0206
	Edge, Average: 0.0178 ± 0.0032						
#3	center 1	2.450	160.930	68964.767	5.70	39.310	0.0254
	center 2	1.780	117.230	68782.735	5.70	39.206	0.0255
	Center, Average: 0.0255 ± 0.0001						
	edge 1	4.550	80.920	254714.53	5.20	132.452	0.0075
	edge 2	4.510	118.360	172611.52	5.20	89.758	0.0111
	edge 3	2.700	70.320	173933.45	5.20	90.445	0.0111
	edge 4	1.690	36.880	207584.06	5.20	107.944	0.0093
	Edge, Average: 0.0098 ± 0.0023						
Remarks		The reference locations were shown in Figure 3-3.					

The conductivity of three P-40 coatings measured by a 4-point probe.
(Process: 2-stage coating method)

	Region	V(volt)	I (μ A)	Rs	Thickness (μ m)	ρ (cm/S)	σ (S/cm)
#1	center 1	1.930	158.900	5.502E+04	7.20	39.615	0.0252
	center 2	1.830	184.560	4.492E+04	7.20	32.340	0.0309
	Center, Average: 0.0281 $\pm$ 0.0028						
	edge 1	2.690	121.460	1.003E+05	6.20	62.203	0.0161
	edge 2	2.240	100.340	1.011E+05	6.20	62.699	0.0159
	edge 3	3.780	211.960	8.079E+04	6.20	50.087	0.0200
	edge 4	4.460	225.710	8.951E+04	6.20	55.498	0.0180
	Edge, Average: 0.0175 $\pm$ 0.0025						
#2	center 1	1.830	202.810	4.088E+04	8.20	33.518	0.0298
	center 2	2.400	259.520	4.189E+04	8.20	34.352	0.0291
	Center, Average: 0.0295 $\pm$ 0.0004						
	edge 1	2.160	118.920	8.228E+04	7.70	64.179	0.0156
	edge 2	1.950	118.000	7.486E+04	7.70	58.391	0.0171
	edge 3	6.010	406.000	6.706E+04	7.70	52.305	0.0191
	edge 4	3.129	192.340	7.369E+04	7.70	57.482	0.0174
	Edge, Average: 0.0173 $\pm$ 0.0024						
#3	center 1	0.903	73.490	5.566E+04	7.80	43.416	0.0230
	center 2	0.998	78.900	5.730E+04	7.80	44.694	0.0224
	Center, Average: 0.0227 $\pm$ 0.0003						
	edge 1	3.090	122.570	1.142E+05	7.20	82.225	0.0122
	edge 2	3.402	139.440	1.105E+05	7.20	79.575	0.0126
	edge 3	1.810	73.890	1.110E+05	7.20	79.896	0.0125
	edge 4	1.740	68.720	1.147E+05	7.20	82.584	0.0121
	Edge, Average: 0.0123 $\pm$ 0.0003						
Remarks		The reference locations were shown in Figure 3-3.					

Appendix D

The conductivity of a pure PANI deposition and a PANI pellet measured by a 4-point probe

	V(volt)	I (mA)	Rs	Thickness (μ m)	ρ (cm/S)	σ (S/cm)
Pure PANI Coating	9.500E-04	1.230E-05	349.878	30	1.050	0.953
	8.720E-04	1.020E-05	387.271	30	1.162	0.861
	7.500E-03	8.290E-05	409.831	30	1.229	0.813
	Average: 0.88 ± 0.053					
Pure PANI Pellet	2.300E-05	1.290E-05	8.077	508	0.410	2.437
	4.500E-05	2.620E-05	7.781	508	0.395	2.530
	3.610E-05	2.160E-05	7.571	508	0.385	2.600
	Average: 2.5 ± 0.064					

Appendix E

The conductivity of the P-30 pattern after a acid treatment.

	Region	V(volt)	I (mA)	Rs	Thickness (μ m)	ρ (cm/S)	σ (S/cm)
P-30	center 1	0.021	0.036	2.650E+06	3.70	9.804E+02	0.001020
	center 2	0.041	0.070	2.621E+06	3.70	9.697E+02	0.001031
	After Exposure to Acid, Center Region, Average					0.001026 $\pm$ 0.000006(S/cm)	
	Before Exposure to Acid, Edge Region, Average					0.001483 $\pm$ 0.00017	
	Recovery					69%	
	edge 1	0.175	0.026	9.438E+07	3.75	3.539E+04	0.0000283
	edge 2	0.736	0.071	4.696E+07	3.75	1.761E+04	0.0000568
	edge 3	0.083	0.009	4.178E+07	3.75	1.567E+04	0.0000638
	edge 4	0.445	0.040	5.040E+07	3.75	1.890E+04	0.0000529
	After Exposure to Acid, Center Region, Average					0.00005 $\pm$ 0.00001(S/cm)	
	Before Exposure to Acid, Edge Region, Average					0.00083 $\pm$ 0.00034	
	Recovery					6%	