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Process development of polyaniline/photoresist thin films for photolithography

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**PROCESS DEVELOPMENT OF POLYANILINE/PHOTORESIST THIN FILMS
FOR PHOTOLITHOGRAPHY**

A Thesis

Presented to

**The Faculty of the Department of Chemical Engineering
San Jose State University**

In Partial Fulfillment

of the Requirements for the Degree

Master of Science

By

Vijay Mathew Vaniapura

December, 1999

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ABSTRACT

PROCESS DEVELOPMENT OF POLYANILINE/PHOTORESIST THIN FILMS FOR PHOTOLITHOGRAPHY

by Vijay M. Vaniapura

Polyaniline/photoresist formulations were prepared and used to cast thin coatings by spin coating. After sonicating the formulations for one hour, reasonably stable suspensions of polyaniline particles were obtained since polyaniline was not soluble in photoresist. The optimum prebaking temperature and time were determined to be one hour at 70 °C. The polyaniline/photoresist coatings contained between 0 and 40 wt.% polyaniline. The percentage of polyaniline in the formulations was based on total solids and was expected to be the same for the resulting coating. The polyaniline content affected the thickness and conductivity of coatings. The thickness of the coatings varied from 0.9 µm for photoresist alone spun coated at 4000 rpm, to 3.2 µm for 40 wt. % polyaniline spun coated at 2500 rpm. The resulting coating thicknesses varied inversely with the spinning speed and were not affected by the spinning time and the volume of the formulation used. The surface roughness of the coatings increased with the polyaniline content. The conductivity of the coatings varied from 1.75×10^{-6} S/cm with 15 wt. % polyaniline to 6.35×10^{-3} S/cm with 40 wt.% polyaniline. Correspondingly, the polyaniline particles were separated from each other at lower concentrations and connectivity occurred when the polyaniline concentration exceeded 30 wt. %.

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Chapter 1

INTRODUCTION

1.1 Conducting Polymers:

POLYANILINE:

Metals are not unique in their ability to conduct electrical current. Other substances including synthetic organic polymers are capable of moving electrons. Some examples of organic polymers with conductivity greater than 10, 000 Siemens/ meter are: Polythienylene-vinylene, Polythiophene, and Polypyrrole [1]. Polyaniline is the best characterized of these so called “organic metals”.

Conductive polymers combine easy processing lightweight and good mechanical properties with higher conductivity. Conductive polymers are plastics with free electrons, capable of carrying charges. Conducting polymers are mainly classified into two groups: filled polymers and intrinsically conductive polymers.

While conductive polymers are not going to replace metals at the present time, their semiconductor like properties make them attractive for a multitude of electrical applications. The major applications for conductive polymers are in rechargeable batteries, microelectronics and micro tools. But intrinsically conductive polymers possess a combination of undesirable properties such as insolubility in common organic solvents, non-processibility using conventional techniques, instability to air and moisture and lack of mechanical strength.

Polymers that conduct electric current without the addition of conductive substances are known as intrinsically conductive polymers (ICP). Polyaniline is one of

the most important polymers belonging to this group. Polyaniline refers to a family of electrically conducting polymers whose general chemical composition is depicted below[2].

Fig.1.1 General Chemical Structure of Polyaniline

In the past few years considerable interest has focussed on materials that exhibit a unique combination of properties including high conductivity, electronegativity, electrochromism, satisfactory environmental stability, processability and chemical versatility. Polyaniline has been demonstrated in a wide spectrum of applications which include electrodes for batteries and light emitting diodes, electrochromic devices, electrostatic discharge(ESD) protection, and welding of plastics. In addition, for the past

few years the applicability of polyaniline has been demonstrated in a number of lithographic processes[3].

Polyaniline is commercially manufactured by Allied Chemicals. Because of its stability in ambient air polyaniline is a good choice for polymer blends, but its rigid polymeric chains yield gels that are poorly soluble in most common organic solvents. N- Dimethyl propylene urea however will permit preparation of a concentrated (10%) polyaniline solution. The continuous polyaniline strands produced from this solution are as electrically conductive as metals, but retain the low weight of the organic polymer. Polyaniline may also be blended with other polymers such as polyethylene or polypropylene to allow molding of electrically conducting objects. Some polyaniline derivatives that are soluble in m- cresol or xylene may be extruded as conductive films [4].

1.2 Polyaniline composites : conductivity percolation threshold, f_c

A polymer composite consists of two or more components, a selected filler and a polymer binder. The filler acts as a reinforcing agent while the polymer binder holds and protects the filler. These two components do not dissolve in each other but act in concert.

Conductive composites are polymers filled with conductive materials such as carbon black, carbon fibers, metal flakes and so on.

The addition of a conductive filler to a polymer can produce a composite with good bulk conductivity(s). The conductivity of the composites is usually not a linear function of the conductive filler content. At the low filler content range, the conductivity is insensitive to the composition until the percolation threshold is reached. The volume

fraction of the conduction filler at the percolation threshold is called the critical volume fraction, f_c

With increasing filler content, distance between filler particles reduces and with further addition of filler, the particles come in contact with each other and form one, two or three dimensional conductive net works with in the insulating matrix. This is called the percolation threshold, at the percolation threshold the conductivity increased dramatically. The conductivity increased as additional filler is added.

Figure 1.2 Conductivity vs. volume fraction of PANI/PPTA fibers [5]

In Figure 1.2. conductivity vs. volume fraction is of PANI in PANI/PPTA fibers is plotted [5]. The plot indicates the conductivity follows equation (1.1) for f values between 10 – 60%

$$\sigma = \sigma_0 f^\alpha \dots\dots\dots (1.1)$$

Where f is the volume fraction of PANI in the composites, $\alpha = 8.5$ and $\sigma_0 = 1.9 \times 10^{-14}$ The conductivity varies with f and follows equation (1) over a range spanning nearly seven orders of magnitude. [6]

Figure 1.3 Conductivity vs. volume fraction (f) of PANI-CSA at 300K and 10K [6]

Reghu et. al. [7] produced polyaniline composites by blending PANI/ CSA in insulating polymethyl methacrylate (PMMA) in which m – cresol was used as the solvent. It was proposed that the formulation of a self – assembled net work of the PANI-CSA/PMMA composites produced extremely low f_c value of 0.003 (0.3%).

The percolation threshold can be determined by the following equation

$$\sigma(f) = \sigma_T * (f - f_c)^t \quad \dots\dots\dots (1.2)$$

In this equation, σ_T is interpreted as the conductance for each basis unit and “t” is the critical exponent, which is the dimensionality of the transport mechanism.

The composites exhibited a continuous increase of conductivity with filler content in Figure 1.3. conductivity vs. volume fraction (f) of PANI-CSA at 300K and 10K are plotted [13].

Ming Hung Shih [8] determined the conductivity – composition profiles for polyaniline composites and generally classified the profiles into three regions: the region below f_c with a small slope, the sharp slope region near f_c and the region of saturated conductivity at higher concentration.

Figure 1.4. Plot of conductivity vs. f for the PANI-DBSA/PVA, PANI-DBSA/PVP and PANI-DBSA/PAA composite films formulated in water and NMP [7]

1.3 POLYMER COATINGS:

FILM FORMATION PROPERTIES:

Generally polyaniline comes in powder form and it is mixed with photoresist (a solution of phenol formaldehyde novolac resin and diazonaphthoquinone in ethylglycol acetate) to form the polyaniline/photoresist solution. The solution formed is non-homogeneous, in fact it is only a dispersion of polyaniline in the photoresist.

The thin film made from this PANI/PR solution is known to be of inferior quality due to its non uniform distribution of PANI and also the non uniform thickness throughout the film. The non – homogeneity in the PANI/PR solution causes the non uniformity of PANI distribution in the film and the non uniformity in the film thickness.

FILM COATING TECHNIQUES:

Thin solid films of polymeric materials used in various microelectronic applications are usually commercially produced by the spin coating deposition(SCD) process, even though almost all the thin film deposition techniques can be used to make polymer thin films. Spin coating is the most cost effective of all of these techniques. There are mathematical models available to predict the film thickness and film thickness uniformity.

Spin coating deposition is the primary commercial process for forming thin films of the various polymeric materials used in the electronics industry. Yet, very little is known about the fundamental physical process of polymer thin film formation on substrates by SCD which includes hydrodynamics, rheology of polymer solutions,

solvent mass transfer, surface and interfacial phenomena, heat transfer and the interplay of these processes.

The deposition of thin solid polymer films by the SCD process is illustrated in Figure 1.5.

Figure 1.5 Deposition of polymer thin films by the SCD process

A predetermined volume of a viscous solution of the polymer is placed on the flat substrate, such as a silicon wafer, which is then rapidly rotated. The dryness of the resulting films depend on the solvent volatility from the solution and parameters such as initial volume of solution, initial concentration of solids, the substrate temperature relative to the boiling point of the solvent, rotational speed and spinning duration. In most cases the polymer film formed at the end of spinning is not completely dry so a prebake at around a temperature of 70 °C is done before further processing. The as deposited film is therefore usually treated by post spinning bake at a higher temperature or in vacuum to remove any remaining solvent in order to produce a dry solid film [9].

1.4 LITHOGRAPHY

Microcircuit fabrication requires the precise positioning of a number of appropriately doped regions in a slice of semiconductor, followed by one or more interconnection patterns. These regions include a variety of implants and diffusions, cuts for gates and metallizations, and windows in protective cover layers through which connections can be made to the bonding pads. A sequence of steps is required, together with specific layout pattern, for each of these regions[10].

Lithographic processes are used to perform these operations, and are carried out in succession during circuit fabrication. Typically, five to ten complete lithographic steps are required on each wafer. By way of example, a conventional silicon based microcircuit, using bipolar transistors, requires seven separate lithographic processes to

define openings of the buried layer, the isolation wall, the base, the emitter/collector, the ohmic contact, the metallization, and the cover layer. Thus lithographic processes play a central role in microcircuit technology.

The placement of a pattern on a wafer can be done in a single step, typically, however, the process is broken into two separate operations: the generation of a mask and its utilization to define cuts in a large number of wafers. The mask pattern is usually produced by serial exposure, one spatial element at a time. The placement of mask patterns on the wafer is an in house activity, since this must be done on each wafer. It is usually a parallel process, involving many of the spatial elements at a time. Optical printing methods are commonly used, but it does not appear that these will meet the requirements for submicron structures over the long term. The most critical part of the lithographic process is conversion of the layout pattern into a master mask.

Lithography is mainly done by four techniques. A lithography technique using X-rays for the resist exposure is referred to as X-ray lithography, and requires the use of different lithography masks and resists. An alternative solution is offered by applying an electron beam (E-beam) to expose the resist. Since the E-beam can be very finely focused, E-beam lithography is capable of writing the pattern directly into the electron sensitive resist by scanning the E-beam according to the desired pattern. No mask is needed in using this technique of resist exposure, and a very high accuracy of pattern delineation is obtained. Ion beam lithography offers several advantages, but the

sensitivity of the resist used in this type of exposure still needs to be improved.

Unfortunately, both E-beam and ion beam techniques are slow and therefore very expensive[11]. The most important technique used for lithography is the photolithography technique, which is discussed in detail in the following paragraphs.

Pattern transfer by photolithography begins by coating the wafer with a thin film of photosensitive polymer and is referred to as either positive or negative. Positive photoresist is initially insoluble in the developing solution and becomes soluble after the exposure to UV radiation. Therefore, after the development photoresist remains on the wafer where the mask is opaque, while it is removed from the remaining areas. In general, positive photoresists are less sensitive than negative photoresists, but they do provide better lithographic resolution. The photolithographic process using negative photoresist is similar to the process using positive resist, the only difference is that the negative photoresist is initially soluble in the developing solution and becomes insoluble after the exposure to light [12].

Photolithography:

Photolithography is a technique used in IC fabrication to transfer a desired pattern onto the surface on a silicon wafer. The starting point of the photolithographic process is a mask in which clear and opaque areas represent the pattern to be transferred onto the wafer. The mask consists of a thin film material, frequently chromium, deposited and photographically shaped on a high quality glass plate which acts as a mechanical support for the mask. During wafer exposure with visible or ultraviolet light the mask prevents penetration of light through the opaque chromium while allowing radiation to pass

through the clear glass. The chemical structure of photoresist is such that the UV light changes its solubility in a developing solution. The photoresist can then be locally removed from the surface of the wafer during a subsequent developing process. This exposes the underlying material, to further processing in selected areas.

The accuracy of the pattern transfer from the mask to the wafer determines the resolution of the photolithographic process. The higher the photolithographic resolution, the finer the geometrical features that can be patterned onto the wafer.

1.5 MOTIVATION

Conductive polymers have long been considered for use in the electronics industry to make microelectronics devices. And recently conducting polymers are being used to form lithographic resists for integrated circuit fabrication, internal dielectric layers for IC and microelectronic layers, magnetic recording media and other applications. In most of these current and future applications, the polymers must be used in the form of thin solid films deposited onto substrates[3]. The motivation for this thesis comes from the fact that polyaniline is a commercially available conducting polymer that could be used in the lithography processes. There is only little work done on the formation and characterization of polyaniline films.

Yuh Jaw Luo (chemical engineering graduate student) in his experiments with polyaniline/photoresists films demonstrated the feasibility of the formation of thin PANI/PR films and also identified some of the important technical issues.

The main problems occurring during the film formation are:

- (1) Non uniform distribution of polyaniline in the film
- (2) Non uniform thickness of the film
- (3) Adhesion of the film on the substrate

The experiments for this thesis will focus on the correlation between the experimental parameters and the thickness variation and distribution of polyaniline. In addition, the relationship between the process parameters and conductivity of the film will be studied to find the optimum value.

The goal of this project is to develop polyaniline/photoresist thin films with good conductivity and good film characteristics to be used for lithography and to determine the relationship between the process parameters and the film characteristics, such as, thickness variation and conductivity.

1.6 Hypothesis

Polyaniline (PANI) and Photoresist (PR) will form a polymer blend, that can be used to make thin films with good conductivity, uniform thickness and uniform distribution of PANI through out the film.

1.7 Research Objectives:

1. Develop a functional process for polyaniline thin films by optimizing all the important process parameters.
2. Determine the change in conductivity with the change in polyaniline concentration in the blend and the spinning speed.
3. Determine the change in film thickness with the change in polyaniline concentration and the spinning speed.
4. Find the relationship between the volume of the solution used and the film thickness.
5. Observe the polyaniline particle distribution in the film with change in concentration of polyaniline in the blend and the film thickness.

Chapter 2

LITERATURE SEARCH AND REVIEW

1. Spin Coating of Very Thin Polymer Films

Charles W. Extrand [13] spin coated thin films of natural rubber, polystyrene, and poly(methylmethacrylate) on silicon wafers from dilute solutions of toluene and cyclohexane. The films were uniform across the wafers with the thickness ranging from 0.5 to 170 nm. Their average thickness increased with solution concentration and decreased with rotational rate. The thickness was independent of the wafer surface preparation and of the volume of solution applied, but was affected by the solvent used.

Figure 2.1 shows the relationship between the viscosity of the solutions and the concentration. The solutions of polystyrene showed no appreciable change in viscosity with concentration, polymethylmethacrylate increased only slightly, while natural rubber (NR) showed a fivefold increase in viscosity for both toluene and cyclohexane.

The time required to drive the solvent off the film was proportional to the rotational rate. Toluene has higher boiling point and took longer to evaporate than cyclohexane. The solutions showed the same inverse spin rate dependence as the solvents. Similar to the solution viscosities, drying times increased with concentration as seen in Figure 2.2. The drying times for the Polystyrene and PMMA films

increased only slightly with concentration while the effect of concentration on drying times of Natural Rubber films were significant.

Figure 2.1. Solution viscosity μ vs. concentration c for natural rubber NR (Δ) Poly(methylmethacrylate)PMMA ($\circ$), and polystyrene PS ($\square$) in toluene and natural rubber NR ($\diamond$) in cyclohexane[13].

Figure 2.2 Drying time t vs. concentration c at $\omega = 93$ rad/s for NR (Δ), PMMA ($\circ$), PS ($\square$) in toluene, and NR (∇) in cyclohexane.[13]

Natural Rubber films were cast using volumes ranging from 0.03 ml to 0.5 ml. The thicknesses of the films were the same, regardless of the volume. However, the surface was not completely covered with lesser volumes. Thickness of the layers increased with concentration and decreased with rotational rate. An example is shown

in Figure 2.3 for NR in toluene. Although the surface treatment made no difference in the average thickness, the choice of solvent did. NR films made from cyclohexane solutions were roughly twice as thick as those from toluene, Figure 2.4.

Figure 2.3. Reduced thickness e/k vs. NR concentration in cyclohexane, where

$$k = (3\mu/4\rho\omega^2t)^{1/2}, \quad \omega = 93 \text{ rad/s (o)}, \quad \omega = 187 \text{ rad/s (}\Delta\text{)}, \quad \text{and } \omega = 347 \text{ rad/s (}\square\text{)} [13].$$

Figure 2.4. Film thickness e vs. NR concentration in two solvents; toluene (Δ) and cyclohexane ($\diamond$)[13]

The reduced thickness is calculated assuming there is no change in the solution viscosity during the spin coating. Also no evaporation occurs until the solvent flashes off, allowing the comparison of the experimental results and the predicted results.

2. Conducting properties of polyaniline blends

McCormick et al. [14] reported the dc conductivity measurements of mixed samples of polyaniline in the conducting form blended with polyaniline in the insulating form and made conducting subsequent to processing. Emeraldine base polyaniline (PANEB) dissolved in N-methylpyrrolidinone (NMP) and emeraldine base polyaniline doped with camphor sulfonic acid (CSA) but dissolved in NMP and also in dimethyl sulfoxide (DMSO) were mixed. The symbolic notation for these mixtures were $(\text{PANCSA-NMP})_{1-x}(\text{PANEB-NMP})_x$ and $(\text{PANCSA-DMSO})_{1-x}(\text{PANEB-NMP})_x$, respectively. Films obtained were then equilibrated in 1 M HCl for a period of 40 to 60 h and vacuum dried prior to performing conductivity measurements. It was shown that the room temperature conductivity increases with increasing values of x .

Insulating emeraldine base polyaniline was synthesized and a portion of it was dissolved in NMP to obtain a 5% by weight solution. Another portion of the emeraldine base was then doped with CSA to protonate it into the conducting salt form and then dissolved in NMP to obtain a 5% by weight solution. Part of the emeraldine base protonated in CSA was then dissolved in dimethyl sulfoxide (DMSO) to obtain a 5% by weight solution. Samples used in this process were prepared by mixing the pure starting materials in proper volume ratios. Thin films, 10 to 50 μm thick, were prepared by coating the polymer on glass slides. The films were then peeled off by soaking in cold water for a few seconds. The conductivity of the film was then measured using the four point probe.

Figure 2.5. Temperature dependence of the dc conductivity of hydrochloric acid doped emeraldine base polyaniline (PANEB) dissolved in N-methylpyrrolidinone (NMP) and PANEB doped with camphor sulfonic acid (CSA) but dissolved in NMP prepared according to the symbolic notation $(\text{PANCSA-NMP})_{1-x}$ (PANEB-NMP)_x x = 0.0(O); x = 0.2 (□); x = 0.8 (◇) and x = 1.0(Δ) [14].

Figure 2.6. Temperature dependence of the dc conductivity of hydrochloric acid doped emeraldine base polyaniline (PANEB) dissolved in NMP and PANEB doped with camphor sulfonic acid (CSA) but dissolved in dimethyl sulfoxide (DMSO) prepared according to the symbolic notation $(\text{PANCSA-DMSO})_{1-x}(\text{PANEB-NMP})_x$ $x = 0.0$ (○); $x = 0.2$ (□); $x = 0.8$ (Δ); and $x = 1.0$ (●) [14]

Figure 2.5. shows the results of the dc conductivity (σ) plotted as a function of temperature (T) for the pure and mixed samples of PANCSA –DMSO and PANEB-NMP. While in Figure 2.6. conductivity for the pure and mixed samples of PANCSA-DMSO and PANEB-NMP are plotted as a function of temperature. In both Figures 2.5. and 2.6. the conductivity plotted logarithmically against $T^{-1/2}$ show an approximately linear behavior in the temperature range above 100K.

The temperature dependence was correlated using the equation

$$\sigma(T) = \sigma_0 \exp [-(T_0/T)^{1/2}]$$

where σ_0 is the pre-exponential factor, the finite temperature conductivity and T_0 is a parameter representing the potential barrier for electrons to hop between chains and a measure of the degree of disorder. Deviations from this model are seen at temperatures below 50 K since reduced thermal excitations lead to increased localization of charges along the polymer chain making them unable to contribute towards macroscopic conductivity. From Figure 2.6. and Figure 2.7. it can be seen that the conductivity in the pure and mixed samples decreased by about three orders of magnitude. This is another indication of increased localization as the temperature is lowered.

McCormick et al. have shown that the room temperature conductivity of PANCSA NMP and PANCSA DMSO films can be enhanced by making polyblends of these polymers with PANEB DMSO. The methodology discussed in this article for preparing polyblends of polyaniline can be suitably extended to include other functionalized protonic acids and solvents.

3. Electrical properties of a new polymer / photoresist composite

Paolo Bruschi and Andrea Nannini[15] proposed a new technique for growing thin films of conducting polymer with arbitrary geometry on substrates compatible with the microelectronic technologies. The new procedure utilized commercial photoresist patterns properly modified in a way to make them suitable for the oxidation of a large class of monomers. The technique was tested with pyrrole, obtaining thin films of a composite material (pyrrole/photoresist) with high conductivity. The new material was optically, morphologically, and electrically characterized. Four point probe resistors were used to measure the resistance as a function of temperature.

The proposed method for the growth of polymeric stripes on various substrates were based on the following steps: (1) a metallic film (typically copper) is deposited on the substrate; (2) the desired geometry is defined with a standard photolithographic technique; (3) the metal is chlorinated to convert it into an oxidizing salt capable of promoting the polymerization of the monomer; (4) the structures are exposed to vapors of the monomer; (5) finally, a rinse is performed to eliminate the excess of oxidizing salt. Commercial positive photoresist and pyrrole monomer were used for the experiment. The resulting pyrrole/photoresist films were morphologically and electrically characterized. They exhibited good adhesion and stability. The characteristics of the polypyrrole/photoresist films were compared with pure polypyrrole films.

The morphological characterization consisted of thickness measurements using a Tencor Alfastep 200 stylus profilometer. The current – voltage measurements were performed for various temperatures on an interval of 25-373K. The I-V curves result rectilinear in the whole interval of investigated temperatures as seen in Figure 2.7. The logarithm of the values of the normalized conduction is shown in Figure 2.8. as a function of $T^{-1/2}$

Figure 2.7. Current vs. Voltage characteristics at various temperatures[15]

Figure 2.8. Linear behavior of the logarithm of the normalized conductance as a function of the inverse of the square root of the temperature for the composite material(upper plot) and polypyrrole (lower plot).[15]

The resistance of polypyrrole/photoresist resistors was monitored over a period of 80 days in order to characterize the time stability of the material. In Figure 2.9, the post deposition resistance of samples stored in air and nitrogen is shown. The curves are normalized to the respective initial resistance values. It can be observed that the rate of increase in resistance was not dramatically different between samples maintained in ambient and inert atmospheres.

Figure 2.9. Post deposition resistance variations of polypyrrole/photoresist thin film resistors kept in nitrogen (A,B) and in ambient air (C,D).[15]

In this article, a new method for depositing thin films of a blend made up of polypyrrole and commercial phototresist was described. The films were highly conducting, demonstrating that a doping process occurred during deposition. Blending polypyrrole with photoresist resulted in improved stability, especially in ambient air.

Chapter 3

EXPERIMENTAL PROCEDURES

3.1 Preparation of Polyaniline / Photoresist thin films

Polyaniline (Allied Signal Inc.) and commercial positive photoresist were used as received to prepare the blend. Polyaniline came as a dark green powder with a conductivity of 2-4 S/cm and particle size ranging from 3-100 microns. The photoresist used was a mixture of Ethyl 3-Ethoxypropionate (60-80 %), Modified Novalac resin (1-27 %) and Methacrylic Methacrylate copolymer (3-6 %). This photoresist consisted of 33.3 % solids and the rest volatile liquids. For this study the weight percent of polyaniline in the polyaniline/photoresist blend was calculated as the percentage of polyaniline with respect to the total solids in the blend. The formula used for the calculation is given below, Polyaniline/photoresist samples with 5 to 40 weight % polyaniline were prepared. The composition of each sample is given in Table 3.1, and is based on the weight of the solids in the solution. The equation use to calculate the wt.% was,

$$\text{Wt. \% polyaniline} = x / (x + 0.333y)$$

where x is the weight of polyaniline in the blend and y is the weight of photoresist in the blend

Table 3.1 Composition of the polyaniline/photoresist blend and film.

Wt. % Polyaniline in film	Weight of PR (gm)	Weight of Pani (gm)	Wt. % of Polyaniline in the formulation
5	1.00	0.0173	1.7
10	1.00	0.0367	3.5
15	1.00	0.0582	5.5
20	1.00	0.0825	7.6
25	1.00	0.11	9.9
30	1.00	0.1414	12.38
35	1.00	0.1776	15.06
40	1.00	0.22	18.03

Polyaniline and photoresist were mixed in an opticlear vial (10 cm diameter, VWR No. 66012-985) using sonic vibration at room temperature in the absence of light. The mixing time for each concentration was determined by observing the settling time. No settling was visible in the first 10 minutes of standing with the samples that had been mixed for one hour.

A known volume (0.2941 ml) of polyaniline / photoresist blend was used to prepare the thin film using spin coating. VWR brand Micro Cover Glasses (25 mm diameter, catalogue no. 48382-085) of 25 mm diameter were used as the substrate. Glass substrates were used as received without performing any cleaning procedure before deposition. Spinning speed from 1500 rpm to 4000 rpm were used to prepare the samples.

The resulting thin films were prebaked to remove the excess solvent before further measurements were done. The optimum conditions of time and temperature for prebaking were determined by measuring the adhesion of the film on the substrate.

The scotch tape test was used to determine the adhesion of the films to the substrate. This test was done by adhering a piece of scotch tape onto the film and pulling it off quickly.

The amount of film present on the scotch tape was used as a measure of the adhesion of the film to the substrate.

3.2 Film Characterization

Thickness of the film was measured using a TENCOR Alpha Step 100, Profilometer. The Alpha-Step has two modes of operation; automatic and manual. In automatic mode the instrument automatically levels itself with respect to the sample and records a scan without interruption. The horizontal magnification switch was set to 50X and the chart recorder showed distinct step heights. To measure the thickness, each sample was scratched with a razor blade, and placed in the instrument with a step free area of 0.5 mm between the stylus tip and the first step on the sample. The stylus tip was dragged across the scratch to determine the thickness. The difference in step height, between the scratched area and the unscratched area, was multiplied with the scale chosen, to obtain the thickness.

The conductivity of the samples were measured using a Minirosin four point Probe with a DC current source (Model HP 6177C), multimeters Model HP 3457 A and Model HP 3458 A for current and voltage respectively.

Figure 3.1. In line four point probe

The current and the voltage were measured at three different locations for each sample as indicated in Figure 3.2.

Figure 3.2. The three locations on the coatings where the conductivity was measured.

The sheet resistance, R_s was calculated using the formula, $R_s = 4.53 (V/I)$, where V is the measured voltage, I is the measured current and 4.53 is the factor

accounting for the probe spacing. The sheet resistance was converted to resistivity, ρ , multiplying by the thickness (t) of the film, $\rho = (Rs)(t)$

The conductivity s is the inverse of the resistivity.

3.3 Polyaniline Particle Distribution

An optical microscope was used to observe the distribution of the polyaniline particles in the polyaniline/photoresist thin coatings. Photographs were taken using 200 X magnification.

Chapter 4

RESULTS AND DISCUSSION

4.1 Preparation of Polyaniline/Photoresist Blend

Like most of the conductive polymers, polyaniline also has the disadvantage of poor processibility, therefore, the preparation of a stable formulation for use in device processing is not straightforward. The formulations prepared contained between 5 to 40 wt.% polyaniline with respect to total solids in the blend. These formulations were mixed using sonic vibration and the mixing times ranged from 15 min for lower solids content to 2 hours for higher solids contents. These formulations were inspected at 5 minute intervals for two hours to determine the settling behavior. The data obtained are listed in Table 4.1. The required sonication time for each composition was obtained by observing the settling behavior of polyaniline particles.

All the formulations were well mixed and stable after standing for up to 10 minutes. After 10 minutes, particle settling was detected. The 5, 10 and 15 wt. % polyaniline blends were sonicated for 60 minutes and revealed no settling during 15 minutes of standing. With 30 min and 60 min sonication the 20 wt.% blends revealed no settling during the first 10 minutes of standing. The 25 % and 30 wt. % polyaniline blends were mixed for 30 min, 60min and 120min. All the blends were stable for 10 minutes before settling was observed. After 24 hours, all the polyaniline particles were completely settled in all the formulations. This demonstrated that the formulations were unstable and settled slowly with time. Therefore, all the polyaniline/photoresist blends

prepared for this study were sonicated for 1 hour irrespective of the contents and thin films were made within 10 minutes.

The settling behavior of polyaniline/photoresist blends for the first 2 hours of standing is given in Table 4.1

(a) Immediately after mixing

(b) After 8 min of standing.

(c) After 15 min of standing

(d) After 20 min of standing.

(e) After 30 min of standing.

(f) After 2 hours of standing.

Figure 4.1 (a- f) Appearance of Polyaniline/Photoresist Blend on Standing After Sonication

Table 4.1 Mixing Times for Polyaniline/Photoresist Blend.

PANI %	Mixing Time (min)	Time(min)							
		5	10	15	20	30	60	120	24 hours
5	15	N	S	E	E	E	E	E	C
	20	N	N	S	E	E	E	E	C
	30	N	N	S	E	E	E	E	C
	60	N	N	N	S	E	E	E	C
10	20	N	S	E	E	E	E	E	C
	30	N	N	S	E	E	E	E	C
	60	N	N	N	S	E	E	E	C
15	30	N	N	S	E	E	E	E	C
	60	N	N	N	S	E	E	E	C
20	30	N	N	S	E	E	E	E	C
	60	N	N	S	E	E	E	E	C
25	30	N	N	S	E	E	E	E	C
	60	N	N	S	E	E	E	E	C
	120	N	N	S	E	E	E	E	C
30	30	N	N	S	E	E	E	E	C
	60	N	N	S	E	E	E	E	C
	120	N	N	S	E	E	E	E	C

N = No particle settling observed, S = some particle settling observed, E = extensive particle settling, and C = completely settled

4.2 Factors Affecting the Film Thickness

In general, the thickness of the polymer coating prepared by spin coating on a glass substrate is affected by the spinning speed, spinning duration, solids content in the solution, viscosity of the solution and the volatility of the solvent. In this study, the effect of polyaniline content in the formulation, volume of formulation used for coating, spinning speed and spinning duration on the film thickness were determined.

The thickness of the polyaniline/photoresist coatings was found to vary with the polyaniline content in the solution. Polyaniline/photoresist thin coatings were prepared which contained 5 to 40 wt.% polyaniline. All the formulations were sonicated for one hour and the coatings were prepared using ≈ 0.3 ml of polyaniline/ photoresist formulation with a spinning time of 40 seconds. The coatings were cast using spinning rates ranging from 1500 rpm to 4000 rpm and the coating thickness was found to decrease with the increase in spinning speed. To determine the effect of polyaniline content on the film thickness, specimens prepared using a spinning speed of 2500 rpm for 40 seconds were selected. The thickness vs. polyaniline content in the blend is tabulated in Table 4.2

Table 4.2 List of Thickness of The Coatings (2500 rpm, 40 sec.).

Polyaniline Content in the formulation Wt. %	Thickness μm
0	0.9
5	1.2
15	1.4
25	2.2
30	2.4
35	2.8
40	3.2

Polyaniline Content vs. Film Thickness

Figure 4.2 Plot of Coating Thickness Against The Polyaniline Content in The Coating.(2500 Rpm, 40 Sec.)

The thickness of the coatings varied from 0.9 μm for photoresist without polyaniline spun coated at 4000 rpm to 3.2 μm to 40 wt.% polyaniline spun coated at 2500 rpm. As we can see in Figure 5.2, the response is quite linear and the thickness increases 0.36 μm for each 5 wt. % increase in polyaniline content for a spinning speed of 2500 rpm and a spinning time of 40 seconds. Charles W. Extrand (13) reported similar results, where the film thickness for thin films of polystyrene and natural rubber in various solvents increased with the solids content of the solution.

The thickness of the polyaniline/photoresist coatings on glass substrate spun coated at 2500 rpm for 40 seconds with different polyaniline contents, can be by Equation 4.1

$$\delta = m * f + c \quad \dots\dots\dots (4.1)$$

Where, δ = film thickness in micrometers f = weight fraction of polyaniline in the formulation, and m and c are the slope and intercept in the thickness vs. polyaniline content graph respectively. From Figure 4.2, m and c are calculated to be 5.611 and 0.9 respectively. Therefore, for these conditions, Equation 4.1 can be rewritten as

$$\delta = 5.611 \pm 0.37 (\mu\text{m}/\text{rpm}) * f + 0.9 (\mu\text{m}) \quad \dots\dots\dots (4.2)$$

The volume of polyaniline/photoresist blend placed in the glass substrate had a small effect on the film thickness. The effect of volume on film thickness was studied using 15%, 25% and 35% polyaniline formulations. All the films were prepared using a spinning speed of 2000 rpm and spinning time of 40 seconds. The film thickness was found to vary slightly with the volume of substrate placed on the glass substrate. The experimental results are summarized in Table 4.3

Table 4.3 Summary of the Volume vs. Thickness Experiments

Wt % of polyaniline in the formulation.	Minimum volume required to cover the entire surface (ml)	Range of volume used (ml)	Average thickness μm
15	0.18	0.18 – 0.26	1.6
25	0.23	0.23 – 0.32	2.2
35	0.28	0.28 – 0.38	2.9

Similar results were obtained irrespective of the polyaniline content in the formulations. Once the solution placed on the substrate was sufficient to cover the whole substrate, further addition of solution did not affect the thickness. The minimum volumes needed to cover the substrate, (25 cm diameter), completely were 0.176 ml. for the 15 wt.% blend (1.5 μm to 1.6 μm thickness), 0.235 ml. for the 25 wt. % polyaniline blend (2 to 2.2 μm thickness) and 0.28 ml. for the 35% wt. % polyaniline blend (2.8 μm to 3.0 μm thickness). The excess volume placed on the substrate spun off the substrate and had little effect on the thickness of the film. The experimental results in detail are given in Appendix A.

Spinning speed and spinning duration have the biggest effect on the film thickness. The effect of spinning time was determined for 10 wt. % and 25 wt. % polyaniline formulations. All the films were prepared using a spinning speed of 2500 rpm, 0.294 ml of the formulation and four different spinning times 30, 40, 50 and 60 sec. The formulations were sonicated for 30 minutes prior to the coating process.

As expected, with the increase in spinning time, the thickness of the film decreased. The resulting thicknesses are tabulated in Table 4.4 and plotted in Figure 4.3.

Figure 4.3 Plot of Film Thickness Against Spinning Time for 10 Wt. % and 25 Wt. % Polyaniline/ Photoresist Coatings.

Table 4.4 List of Coating Thicknesses for Variations in Spinning Times for The 10 Wt.% and 25 Wt.% Polyaniline Coatings.

Spinning time (sec.)	Thickness (μm)	
	10 wt. % Pani	25 wt. % Pani
30	1.2	2.3
40	1.1	2.1
50	1.1	2.0
60	1.0	2.0

The effect of spinning speed on thickness is discussed in section 4.4.1 under the characterization of polyaniline photoresist coatings.

4.3 Optimization of Prebaking Time and Temperature

The polyaniline/photoresist coatings were prebaked to remove the excess solvents before further processing. The prebaking temperature and time were optimized by determining the adhesion of the coatings on the glass substrate. The scotch tape test was used to determine the adhesion of the coatings. The amount of film present on the scotch tape was used as a measure of the adhesion to the coatings to the substrate.

To determine the prebaking conditions, polyaniline/photoresist coatings were prebaked using temperatures 50 °C, 70 °C , 90 °C for different durations of time. All the samples prepared for this test contained 25 wt. % polyaniline in the formulation and were sonicated for one hour. The coatings were prepared using a spinning speed of 2500 rpm for 40 seconds. The results of the scotch tape test are tabulated in Table 4.5.

Table 4.5 Scotch Tape Test Results for Polyaniline/Photoresist Coatings with Different Prebake Treatments.

Temp °C	Time (min.)	Adhesion
90	15	Poor
70	15	Poor
70	30	Poor
70	60	Good
50	30	Poor
50	60	Good
50	90	Poor

Only two sets of conditions passed the scotch tape test, 70 °C for 60 min. and 50 °C for 60min. When other prebaking conditions were used, approximately more than 10 % of the coating lift off due to poor adhesion and these conditions were considered a failure. Therefore all the subsequent samples used for thickness and conductivity measurements were prebaked at 70 °C for 60 minutes.

Polyaniline/Photoresist Coatings Characterization

4.3.1 Thickness

Thicknesses of the polyaniline/photoresist coatings on glass substrate were measured using the TENCOR Alpha Step 100, Profilometer. Thicknesses of each of the prepared samples were measured and are tabulated in Table 4.7. The measured values of thickness were used to determine the relationship between the spinning speed and

thickness of the coatings. While many measurements were made for this study, only a few pictures of the traces were selected to be included in this report.

Figure 4.7. (a) The Trace of Polyaniline/Photoresist Coatings Using The Alpha Step Profilometer (0 Wt. %, 3000 Rpm)

Figure 4.7. (b). The Trace of Polyaniline/Photoresist Coatings Using The Alpha Step Profilometer (5 Wt. %, 3000 Rpm)

Figure 4.7. (c). The Trace of Polyaniline/Photoresist Coatings Using The Alpha Step Profilometer (15 Wt. %, 3000 Rpm)

Figure 4.7. (d). The Trace of Polyaniline/Photoresist Coatings Using The Alpha Step Profilometer (25 Wt. %, 3000 Rpm)

Figure 4.7. (e). The Trace of Polyaniline/Photoresist Coatings Using The Alpha Step Profilometer (35 Wt. %, 3000 Rpm)

The profilometer traces can generally be divided into three regions, two film regions and a glass region. In the film regions, the trace had many ups and downs while in the glass region it was a straight line. The traces for the thickness measurements also provided the surface roughness of the polyaniline/photoresist coatings. A comparison of the traces showed a smooth surface for pure photoresist coatings and a very rough surface for 35 wt. % polyaniline coatings. There was an increase in roughness with the increase in polyaniline content in the polyaniline/photoresist formulation. The large spikes are overshoots and not necessarily the size of a particle.

Table 4.6. Coating Thicknesses Produced by Different Spinning Speeds.

Spinning speed rpm	Thickness (μm)					
	0 wt % PANI	5 wt % PANI	15 wt % PANI	25 wt % PANI	30 wt % PANI	35 wt % PANI
1500	1.1	1.2	1.5	2.4	2.6	3.2
2000	1.0	1.2	1.4	2.3	2.6	3.0
2500	0.9	1.2	1.4	2.2	2.4	2.8
3000	0.85	1.0	1.3	2.2	2.2	2.6
3500	0.75	1.0	1.2	2.0	2.2	2.2
4000	0.70	0.9	1.2	1.8	2.0	2.2

As seen in Figure 4.5, the thickness of the polyaniline/photoresist coatings varies inversely with the spinning speed, and increases with polyaniline content in the formulation. The thickness variation with spinning speed for each concentration can be fitted by Equation 4.1. Where f is the spinning rate, m and c are the slope and intercept of the thickness vs. spinning speed plot respectively. The slope and the intercept of thickness vs. spinning speed graph for each polyaniline content in the formulation are tabulated in Table 4.7

Figure 4.5 Plot of Thickness Vs. Spinning Speed For Various Polyaniline Contents In The Formulation

In general, the effect of spinning speed on thickness is greater on the formulations with higher polyaniline content.

Table 4.7 Slopes and Intercepts of the Plots in Figure 4.5

Wt. % of polyaniline in the formulation	Slope $\mu\text{m}/\text{rpm}$	Y – axis intercept μm
0	$-1.6 \text{ E } -4 \pm 1.93*10^{-7}$	1.35
5	$-1.45 \text{ E } -4 \pm 2.196*10^{-7}$	1.45
15	$-1.75 \text{ E } -4 \pm 1.59*10^{-7}$	1.65
25	$-1.75 \text{ E } -4 \pm 0.78*10^{-7}$	2.8
30	$-2.69 \text{ E } -4 \pm 4.48*10^{-7}$	3.0
35	$-4.18 \text{ E } -4 \pm 2.53*10^{-7}$	3.75

The thickness variation within a sample was also determined using coatings prepared at 3000 rpm for different polyaniline contents. To determine the thickness variations within a coating, measurements were made at eight different locations along the coating as shown in Figure 4.6

Figure 4.6. Locations of Thickness Measurement to Determine the Variation of Thickness within A Specimen.

The outer region of the samples was generally thicker and then the thickness decreased towards the center of the substrate. This study revealed that at lower polyaniline contents, the thickness did not vary substantially within the film. The thicker films showed substantial variations in the thickness along the locations where the measurements were made. The data obtained is plotted in Figure 4.7. In this plot, the x-axis represents the locations where the measurements were made, where 0 is the center and -12.5 and 12.5 represents the edges, while the y-axis represents the corresponding thicknesses.

Figure 4.7. Plot of Thickness Variation Within The Wafer (Diameter = 25 Mm).

4.3.2 Conductivity Measurements

Conductivity and photoreactivity are two of the desired properties of the polyaniline/photoresist coatings for generating photolithographic patterns . In this study, the conductivity of polyaniline/photoresist coatings with various polyaniline contents in the formulation was determined. The conductivity of the coatings was measured using a four point probe and the measured voltage , current and calculated conductivity (σ) values are tabulated in Table 4.8. Applied voltage and current were measured at arbitrary points (a,b,c,d) on the coatings. The conductivity (σ) of the coatings from Table 4.8. are plotted against the polyaniline content in the formulations in Figure 4.8.

Table 4.8. Conductivity Measurements of Polyaniline/Photoresist Coatings

Wt. % * Pani	Spinning speed rpm	Voltage V	Current I(μ A)	Sheet resistance $10^{-9}R_s$ ($\Omega/$)	Resistance ρ (Ω -cm)	Conductivity $10^6\sigma$ (S/cm)
15	1500	1.408	.001	6.378	956700	0.104
15	2000	1.5237	.001	6.9	966000	0.103
15	2500	1.7892	.001	8.1	1134000	0.880
15	3000	1.89	.001	8.56	1112800	0.890
15	3500	2.0326	.001	9.2	1288000	7.7
15	4000	2.1774	.001	9.86	1183200	0.845

Wt. % Pani	Spinning speed rpm	Voltage V	Current I(μ A)	Sheet resistance $10^{-9}R_s$ ($\Omega/$)	Resistance ρ (Ω -cm)	Conductivity $10^6\sigma$ (S/cm)
25	1500	1.482	.001	6.65	1596734	0.626
25	2000	1.937	.001	8.77	2017813	0.495
25	2500	2.0	.001	9.06	1993200	0.501
25	3000	2.017	.001	9.13	1792114	0.558
25	3500	1.66	.001	7.51	1503985	6.649
25	4000	2.072	.001	9.386	1690596	0.595

Wt. % pani	Spinning speed rpm	Voltage V	Current I(μ A)	Sheet resistance $10^{-9}R_s$ ($\Omega/$)	Resistance ρ (Ω -cm)	Conductivity $10^6\sigma$ (S/cm)
30	1500	0.392	.001	4.71	737000	2.16
30	2000	0.82	.001	3.71	83600	1.03
30	2500	1.04	.001	1.77	860000	0.887
30	3000	0.74	.001	3.35	461697	1.35
30	3500	0.084	.001	0.38	964600	11.96
30	4000	0.95	.001	4.53	1130400	1.162

* wt. % of polyaniline with respect to the total solids in the formulation.

Wt. % pani	Spinning speed rpm	Voltage V	Current I(μ A)	Sheet resistance $10^{-9}R_s$ ($\Omega/$)	Resistance ρ (Ω -cm)	Conductivity $10^6\sigma$ (S/cm)
35a	1500	0.256	1.473	0.1737	55.584	3.96
b		0.290	0.792	0.366	117.2	1.8
c		0.220	0.582	0.378	120.96	1.82
d		0.798	1.838	0.434	138.9	1.59
35a	2000	0.595	0.595	0.445	133.5	1.65
b		0.413	0.413	0.356	106.8	2.07
c		0.933	0.933	0.44	132	1.67
d		0.026	0.026	0.730	219	1.03
35a	2500	0.461	0.461	0.665	186.2	1.118
b		0.474	0.474	0.645	180.6	1.22
c		0.24	0.24	1.29	361.2	0.610
d		0.646	0.646	0.764	213.92	1.03
35a	3000	0.7	1.0	3.171	964.86	1.03
b		0.7422	1.028	3.27	850.2	1.76
c		1.28	0.989	5.8628	1524.6	0.656
35a	3500	0.9687	1.062	0.9121	200.62	5.0
b		0.67	0.984	0.6808	149.72	7.2
c		1.72	0.617	2.787	633.12	1.58
35a	4000	1.328	0.7	1.897	1890.69	0.529
b		1.74	0.476	3.65	804.2	1.24
c		1.09	0.348	3.312	689	1.45
d		0.058	1.00	0.58	578.03	1.73

Wt. % pani	Spinning speed rpm	Voltage V	Current I(μ A)	Sheet resistance $10^{-9}R_s$ ($\Omega/$)	Resistance ρ (Ω -cm)	Conductivity $10^6\sigma$ (S/cm)
40a	1500	0.82	5.578	0.673	195.22	5.12
b		0.4276	3.578	0.541	156.89	6.37
c		0.728	4.473	0.737	213.73	4.67
40a	2000	0.589	6.867	0.388	120.28	8.31
b		0.6814	5.578	0.553	171.43	5.83
c		1.073	7.405	0.656	203.36	4.91

Conductivity vs. Polyaniline Content

Figure 4.8. Plot Of Conductivity against Polyaniline Content in the Formulation. (% of Solids)

For comparison, the conductivity of a polyaniline coating, unblended, was 0.88 S/cm and of a polyaniline pressed pellet was 2.5 S/cm[16]. The conductivity values reported in [16] were higher than the corresponding values in this study due to the difference in thickness of the coatings. The conductivity of the polyaniline/photoresist coatings with lower polyaniline content was negligible and increased rapidly when the polyaniline weight percentage with respect to the solids in the formulation was greater

than 30. At higher polyaniline contents, the increase in conductivity was enormous. In Figure 4.8. it can be seen that the critical weight fraction, the composition where the conductivity becomes detectable and significant, is between 0.3 and 0.33. Formulations with less than 0.33 polyaniline weight fraction produce coatings that are practically nonconducting. As is evident from Table 4.8., for all the specimens, there was only a small variation in the conductivity values within a particular film and also with increase in thickness of the polyaniline/photoresist coatings. This small variation was most likely due to the uneven distribution of polyaniline particles in the film.

Comparison of these results with those presented in Yuh –Jaw Luo's thesis [16] showed some differences in the conductivity values. These differences are mainly attributed to the difference in the processes and coating thicknesses. For example in this study, 40 wt. % polyaniline coating had a thickness of 3.2 μm and a conductivity of 0.0056 S/cm compared to Luo's coatings, which had a thickness of 7.6 μm and a conductivity of 0.027 S/cm.[16].

4.3.3 Distribution of Polyaniline in Polyaniline/Photoresist Coatings

The distribution of the polyaniline particles in the polyaniline/photoresist coatings depends on the effectiveness of the mixing and the polyaniline content in the formulation. To determine polyaniline particle distribution, the coatings were inspected using an optical microscope. Photographs were taken at 200 times magnification and a few selected photographs are presented below in Figure 4.9

Figure 4.9. Distribution of polyaniline in polyaniline/photoresist: (a). 40 wt. %, 2000rpm;
(b). 40 wt. %, 3000 rpm

Figure 4.9.(Contd.) Distribution of polyaniline in polyaniline/photoresist: (c). 35 wt. %, 2500 rpm; (d). 25 wt. %, 2500 rpm

In Figure 4.9(a).it can be seen that the polyaniline particles are distributed fairly evenly in the coating with the 40 wt. % polyaniline/photoresist formulation. The surface of the substrate was covered with polyaniline particles and there were no significant voids and cracks. In Figure 4.9.(b). a photograph of polyaniline/photoresist coating containing 40 wt. % polyaniline is presented. As can be seen, the surface coverage is also complete; however, there were white areas showing no polyaniline in the coating. A comparison of these two photographs shows that thicker film (a) has better polyaniline particle distribution than the thinner film (b) for the same formulation. The coatings with the higher polyaniline particle content have a more even distribution of the particles and this situation makes the coating conducting. However, these thicker films were not good for lithographic applications because they had poor adhesion to the substrate in addition to the poor response to ultraviolet light. Figure 4.9 (c). and 4.9(d). respectively show the photographs of polyaniline/photoresist coatings containing 35 wt.% and 25 wt. % polyaniline spun coated at 2500 rpm. By comparing these two photographs, it can be seen that more complete coverage of polyaniline particles and more connective paths were attained with higher polyaniline contents in the formulation.

By comparing Figures 4.9(e). and 4.9(f)., it can be seen that with less polyaniline, the particles were separated from one another and therefore do not form connective paths throughout the film. This is consistent with the non conductive nature of the films. All the photographs were taken at 200 times magnification, therefore, in the photographs one centimeter represents 50 μ m. The particles sizes were estimated to be 5 – 10 μ m in the coatings with the lower polyaniline content.

Figure 4.9. Distribution of polyaniline in polyaniline/photoresist: (e). 15 wt. %, 2500 rpm; (f). 5 wt. %, 2500 rpm.

Chapter 5

Summary and Conclusions

5.1 Summary

Based on the study the best conditions for polyaniline/photoresist thin coatings for lithography are as follows:

Polyaniline content in the formulation should be 35 wt.% with respect to the total solids to get the optimum thickness, conductivity and reasonably good adhesion to the substrate. The polyaniline/photoresist formulation should be sonicated for one hour at room temperature and the coatings should be prepared within the first ten minutes of standing. The optimum coating conditions were found to be 2500 rpm for 40 seconds.

5.2 Conclusions

In this study the effect of various parameters on the thickness and conductivity of polyaniline/photoresist thin coatings prepared by spin coating were evaluated. The parameters evaluated were: polyaniline content in the formulation, volume of formulation applied for spin coating, spinning speed and spinning time. This study showed that the polyaniline particles in polyaniline/photoresist formulations were not stable for long periods of time and started settling after 10 minutes of standing irrespective of the sonication time and polyaniline content.

The polyaniline content in the formulation and the spinning speed had the biggest effect on the thickness. The formulations prepared for this study had 0 to 40 wt. % polyaniline in polyaniline/photoresist with respect to the total solids. The spinning speeds used were changed from 1500 rpm and 4000 rpm. The thickness of the

polyaniline/photoresist coatings increased with polyaniline content and decreased with spinning speed. The thickness of the coatings varied 0.70 μm for 0 wt. % polyaniline at 4000 rpm to 3.2 μm for 35 wt. % polyaniline at 1500 rpm. The thickness of the coatings did not vary substantially with the volume of the formulation applied on the substrate and the spinning time. The change in thickness with the change in spinning speed was linear. Therefore polyaniline/photoresist coatings with the desired thickness and polyaniline content can be produced by choosing the appropriate value of spinning speed from the thickness vs. spinning speed graph. The best prebaking condition was at 70 $^{\circ}\text{C}$ for one hour. The coatings prepared using these conditions had good adhesion to the substrate.

The highest conductivity achieved was 0.0064 S/cm for the coatings with 35 wt. % polyaniline spun coated at 2000 rpm. The coatings became conducting when the polyaniline content in the formulation exceeded 30 wt. %. The change in conductivity was attributed to the polyaniline particle distribution in the coatings. At lower polyaniline content, the polyaniline particles were separated from one another and there were no connective paths formed to conduct electricity. At higher concentrations the polyaniline particles were in contact to form the connective paths. This study showed that conducting polyaniline/photoresist coatings can be made as thin as 2.0 μm by spin coating 35 wt.% polyaniline at 4000 rpm

The conductivity within a sample varied from one point to another due to poor polyaniline distribution. The reproducibility from wafer to wafer was poor since the polyaniline used for this study was commercial grade polyaniline and the particle size

had varied from 3 μm to 100 μm in the bulk. A higher polyaniline content was needed for good conductivity but at these contents, the adhesion to the glass substrate was poor and the coatings had a rough surface due to the presence of large polyaniline particles. The thickness variation within the wafer was substantial with the higher polyaniline contents, where there was an increase in thickness towards the edges.

Recommendations for Future Study

Considering the results of this study, the following suggestions are made for future study;

Formulation: Filter out the larger polyaniline particles to have a more uniform particle size and to attain a better dispersion of polyaniline in photoresist. Distribution of polyaniline particles is expected to improve with the degassing of the formulation after mixing. A study of the rheological properties of the formulation is suggested to determine the behavior of the formulation during spin coating.

Coatings: All the coatings in this study were prepared on glass substrates, film coatings on bare or oxidized silicon wafers were shown to have better adhesion than on glass[16]. Silicon wafers should be used in future studies. Scanning electron micrographs should be used to study the polyaniline particle distribution and surface roughness of the coatings.

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Appendix A.

Table A.1. Effect of the volume of solution on the film thickness for 15 wt. % polyaniline coatings spun at 2000 rpm for 40 seconds.

No of Drops	Vol. ml	Thickness (μm)
3	0.088	1.4*
4	0.117	1.4*
5	0.147	1.4*
6	0.176	1.5
7	0.205	1.6
8	0.235	1.6
9	0.264	1.6

Figure A.1. Plot of film thickness against volume for 15 wt. % polyaniline blend.

Table A.2 Effect of the volume on the film thickness for 25 wt. % polyaniline coatings spun at 2000 rpm for 40 seconds.

No of Drops	Vol. (ml)	Thickness (μm)
5	0.147	2.0*
6	0.176	2.0*
7	0.205	2.0*
8	0.235	2.0
9	0.264	2.2
10	0.2941	2.2
11	0.3235	2.2

* = Insufficient solution to cover the substrate completely.

Figure A.2. Plot of film thickness against volume for 25 wt. % polyaniline blend.