A Study of Solvent-Rich Environments for Evaporation Rate Control in the Extrusion Spin Coating Process

by

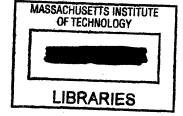
Winston C. Fan

Submitted to the Department of Mechanical Engineering in partial fulfillment of the requirements for the degree of

Bachelor of Science in Mechanical Engineering

at the

MASSACHUSETTS INSTITUTE OF TECHNOLOGY



June 1998

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Abstract

Microlithography is a process used in microchip fabrication to transfer a circuitry pattern onto a silicon wafer. An important step in the process is the deposition of a thin coating oresist from which the lithographic mask is made. The photoresist layer is typically 1 µm thick with a thickness variation of less than 25Å (within 3σ). The current industrial process of spin coating can achieve these specifications. However, these standards are achieved at the cost of wasting 95% of the photoresist applied. Extrusionspin coating is a new coating method that has the potential of wasting as little as 50% of the photoresist applied. Before extrusion-spin coating can be used effectively, however, the coating uniformity must be improved through the reduction of solvent evaporation from the wafer surface. This research project evaluates improvements in coating uniformity resulting from the application of a low to moderate solvent concentration environment. At low dispense volumes of approximately 0.5ml, the standard deviation from the mean of the coating thickness was reduced from 335Å to 56Å with the application of a low solvent concentration environment. At the highest solvent concentration level that can be achieved by the experimental apparatus, the extrusion-spin coating had a deviation comparable to the high dispense volume, traditional spin coating technique. In addition, the extrusion-spin coating also had an efficiency that was more than a magnitude higher than that of the spin coating. This study indicates that extrusionspin coating in a solvent-rich environment is a viable replacement for the spin coating process.

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Nomenclature

B_s	Mass transfer driving force
D	Solvent diffusivity (diffusion coefficient)
g	Mass transfer coefficient
g h	Wet coating thickness
$m^{"}$	Mass of solvent evaporated per unit area
$m_{s,\varepsilon}$	Mass fraction of solvent in the air just above the fluid surface
$m_{s,s}$	Mass fraction of solvent at the surface of a fluid film
Q	Photoresist flow rate
r	Raidal distance from the center of a disk (wafer)
ν	Relative tangential velocity between wafer and extrusion head
w	Extrusion width

Greek

- ρ Density
- v Kinematic viscosity
- Ω Wafer rotation speed

Subscript

as Air-solvent

Dimensionless Numbers

Nu_r Nusselt number
 Pr Prandtl number
 Re Reynolds number
 Sc Schmidt number
 Sh Sherwood number

Chapter 1

Introduction

Improvements in microchips are driven largely by continued circuitry miniaturization. Miniaturization is limited by the capabilities of existing manufacturing processes, particularly in the area of microlithography. Improvements to these processes must attain the same or better process time, quality, and output. In addition, any new process must be relatively more efficient so that its gains will not be outweighed by the exponentially increased cost of the materials needed to achieve an higher resolution. One process in particular to be improved upon is the spin coating process. A new process of extrusion spin coating may be able to attain results superior to that of traditional spin coating. However, several problems need to be resolved before the extrusion spin coating process can become an effective replacement to the current process.

1.1 Microlithography

Microlithography is the process by which micro-electronic devices are manufactured. As shown in Figure 1 [11], it consists of a number of planar processes, each producing a layer

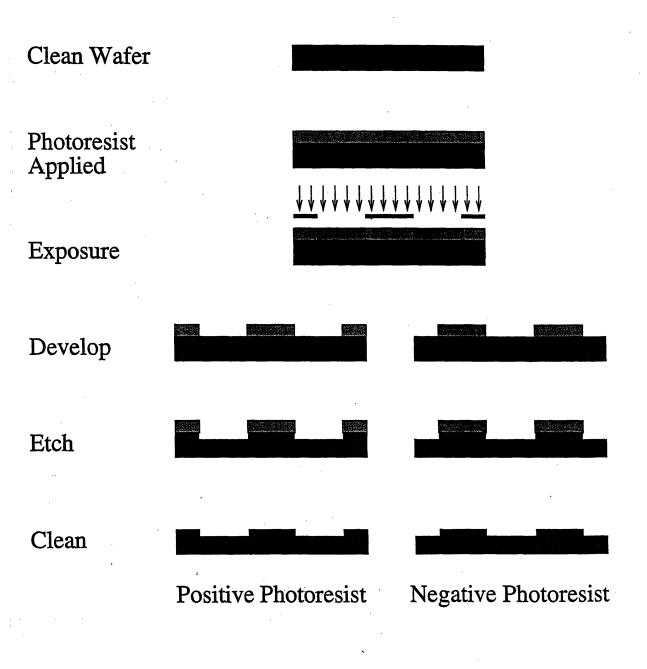


Figure 1. Microlithography process steps.

of circuitry pattern [8]. The first step is the application of a thin layer of light-sensitive film, or photoresist, to the substrate. Photoresist comprises of a polymer in solution in a solvent. A mask containing the circuitry pattern for that level is then placed over the wafer. Irradiation of the film through the mask copies the pattern onto the film. The film is then developed. In the case of positive photoresist, the exposed sections of the coating are removed, while in negative photoresist, the unexposed portions of the coating are removed. Material is then added to to the uncoated areas to form the circuitry. This is done through processes such as etching, deposition, oxidation and doping. Finally, the photoresist is removed from the wafer and the surface is prepared for the next layer.

1.2 Spin Coating Process

Spin coating is the current industrial method used to deposit a film of photoresist onto a wafer. To begin with, just enough photoresist to cover the surface is deposited onto the wafer. The wafer is then rotated at a velocity sufficient to spread the photoresist across the surface. Finally, the wafer is spun at a high speed. During this spinning process, the photoresist thickness approaches its final value as excess photoresist is flung off the wafer surface and the solvent evaporates, leaving the polymer behind. The wafer is then baked to remove the remaining solvent from the polymer.

Current requirements for microchip fabrication demand film thicknesses between 0.5 - $4.0~\mu m \pm 25$ Å. The entire coating process should take no more than 30 to 45 seconds. Spin coating is the only industrial process that can meet these standards.

However, these values are achieved with extreme inefficiency. More than 90 % of the photoresist applied to a wafer is wasted as it is flung off the surface. This represents a wastage of approximately 100 million gallons per year at a cost of 400 million dollars[10]. As new deep UV photoresist is introduced, the cost of photoresist will increase by a factor of five or more. There is a great industrial demand for a process with a marked improvement over spin coating efficiency with comparable values in thickness, uniformity, and coating time. One of the processes currently being considered is the extrusion spin coating process.

1.3 Extrusion Spin Coating

Extrusion spin coating is based on the extrusion slot coating process. In this process, fluid is dispensed through a narrow slot formed by two parallel plates. As shown in Figure 2, a bead of the coating fluid fills the gap between the slot and the substrate. As the substrate moves perpendicular to the slot, the fluid is drawn from the bead to form a thin film on the substrate. The thickness of the coating is governed by the following equation:

$$h = \frac{Q}{wv} \tag{1}$$

where ν is the coating speed, w is the width of the extruded film, and Q is the fluid dispense rate. Figure 3 shows the geometry of an extrusion die [4]. The lips of the die must have a radius of curvature of less than 50 μ m to pin the meniscus of the bead to the leading and trailing edges of the die [3].

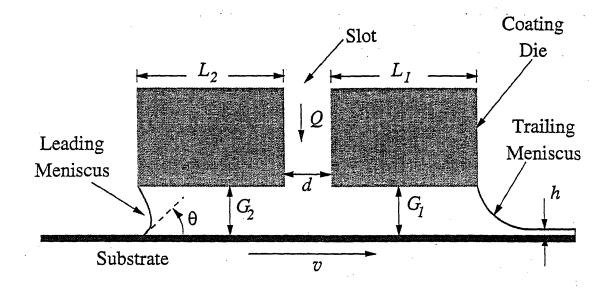


Figure 2. Cross-section of the lips of an extrusion slot coating die with a substrate moving beneath them.

A significant advantage of the extrusion slot coating process is its efficiency. As with all pre-metered coating methods, all the fluid dispensed is used in coating the substrate [5]. The only wastage is in the fluid dispensed to flush bubbles or to reach a uniform flow prior to contact with the substrate. If the extremes of the coating limits are avoided, the number of defects can be kept very low. Finally, the coating time can be adjusted to fit requirements by varying the slot width and the coating velocity. The main disadvantage of the extrusion slot coating process is its inability to coat substrates of varying widths.

Extrusion spin coating is an application of the extrusion slot coating method to the spin coating process [1]. To coat a silicon wafer as represented by the flat disk in Figure 4, an extrusion die much smaller than the radius R of the wafer is used. The extrusion die

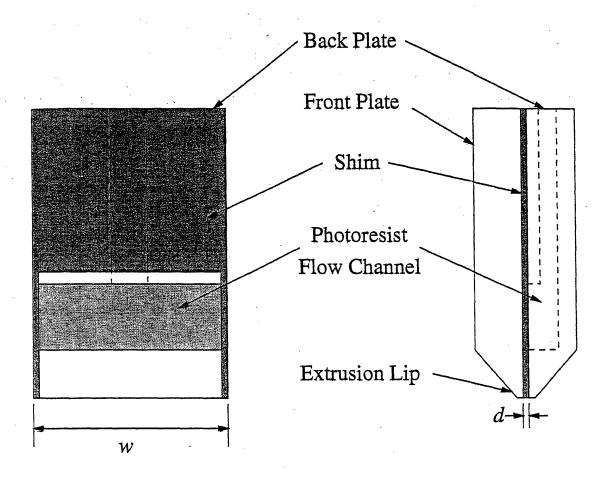
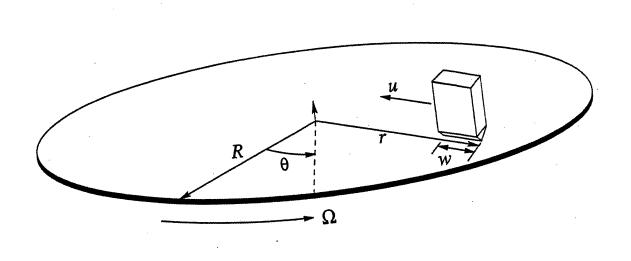


Figure 3. Extrusion die.

is oriented along the diameter of the wafer. The wafer is rotated at an angular velocity Ω while the extrusion die moves toward the center of the wafer at a velocity proportional to the angular velocity of the wafer. The result is a spiral coating that can then be spun at a high velocity to achieve the final coating thickness.

The coating window for the extrusion coating process is bounded by the need to maximize efficiency and coating speed. It is also imperative to limit evaporation during the coating process. Finally, the low flow limit of coatability constrains the maximum coating speed and the minimum coating thickness. As shown in Figure 5[1], coatings of acceptable quality can be made within these boundaries.

The test results produced by Derksen et al. [1] have shown that the extrusion spin coating process can be used to produce uniform coatings at thickness below 1.5 µm in approximately 1 minute at efficiencies of 25% or more. However, as shown in Figure 6, the extrusion spin coating method does not meet the uniformity requirement. The tests have shown that the thickness uniformity is highly dependent on the evaporation during the extrusion coating phase. If evaporation during the coating application phase is reduced or eliminated, the extrusion spin coating process can then meet the uniformity requirement.



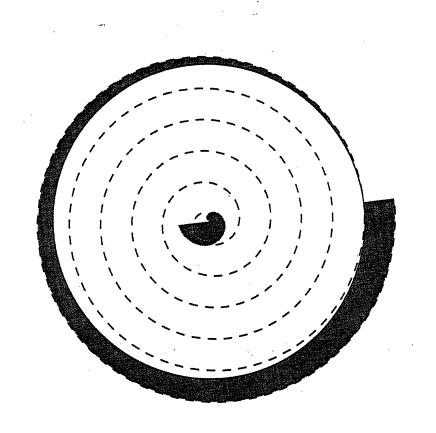


Figure 4. Extrusion-spin coating spiral pattern. Outline of disk (-), edge of spiral rings (--). Shaded regions show wasted photoresist at outer edge and double photoresist thickness at center.

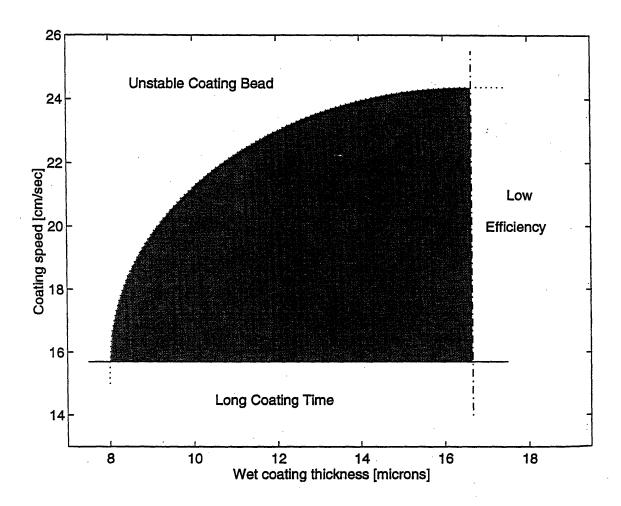


Figure 5. Coating window for extrusion-spin coating. 20 second coating time (-), 25% efficiency (---), bead stability limits ($\cdot \cdot \cdot$) are dependent on the viscosity and other properties of the coating fluid.

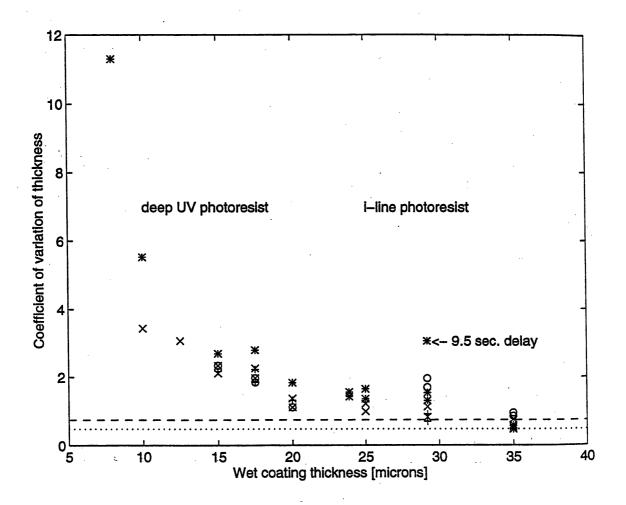


Figure 6. Final (dry) coating thickness uniformity. Coating speed = 6cm/sec (o), 8cm/sec (*), 10 cm/sec (x), 12 cm/sec (+), 14 cm/sec (\otimes), and 16 cm/sec (\oplus). Traditional spin coating is indicated by (--) for I-line photoresist and ($\cdot \cdot \cdot$) for deep UV photoresist.

Chapter 2

Motivation

Coating uniformity remains a serious hurdle to be overcome before extrusion spin coating can be considered a viable replacement for the spin coating process. Since evaporation during the coating phase has the greatest effect on uniformity, this study will concentrate on reducing evaporation from the coating surface.

There are several methods by which to reduce evaporation from the wafer surface. The first method introduces a solvent-saturated environment during the coating phase. The second method is to control the temperature of the photoresist or the wafer and chuck, or both. By reducing the temperature of the fluid and the substrate, the evaporation rate will be likewise limited. The final method reduces convection by ensuring that there is no relative velocity between the wafer and the air directly above the wafer. The second method was discarded because the apparatus is incapable of controlling the external environment, thus making it very difficult to maintain a uniform

temperature in the fluid, chuck, or wafer. The third method was discarded because it would be very difficult to implement such a system in a satisfactory fashion without a major redesign of the apparatus. More importantly, given the low coating velocity, the effect of such a device on the evaporation rate is expected to be rather modest. The solvent-saturated environment was selected for further experimentation because it is expected to have a significant effect on coating uniformity.

2.1 Theoretical Analysis

The mass transfer rate per unit area for evaporation from a spinning disk is [1]:

$$m'' = \frac{0.585D_{as}\rho}{0.6/Sc + 0.95/Sc^{1/3}} \left(\frac{\Omega}{v_{as}}\right) \ln\left(\frac{1}{1 - m_{s,s}}\right)$$
(2)

Where D_{as} is the air-solvent diffusion coefficient, $Sc = v_{as}/D_{as}$ is the Schmidt Number, Ω is the rotational speed of the disk, v_{as} is the viscosity of the solvent-air mixture over the disk, and $m_{s,s}$ is the mass fraction of the solvent at the surface of the fluid film on the disk (determined by the partial pressure of the solvent at the surface). Figure 7 shows the solvent evaporation calculated from Equation 2 for a 25 μ m spiral coated from the edge of the disk to the center. The fluid layer is assumed to consist only of solvent to obtain an upper bound on solvent evaporation. As shown in the figure, the evaporation is nearly an order of magnitude higher at the edge than at the center. The higher evaporation at the edge will result in higher viscosities and greater film thicknesses than those at the center of

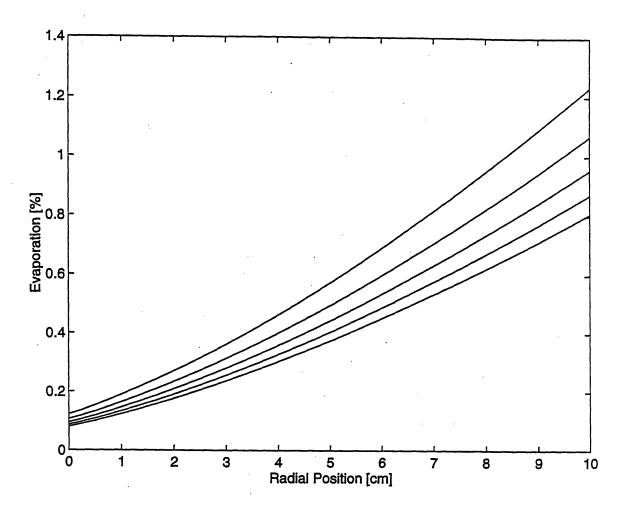


Figure 7. Solvent evaporation for a 25µm thick wet coating for coating velocities of 6, 8, 10, 12, 14 cm/sec (top to bottom).

the disk. Figure 8 shows the effect that evaporation has on the edge of a 20-cm disk with different wet coating thicknesses. Figure 9 shows a map of the final dry coating thickness. Thinner films, which have less solvent to begin with, will be more negatively impacted. Unless solvent evaporation is significantly inhibited, the edge of the wafer will remain thicker than the center, thus affecting the coating's uniformity.

As can be seen from Equation 2, evaporation can best be inhibited by reducing the air-solvent diffusion coefficient. The method chosen is to create a solvent saturated

environment over the wafer. This will reduce the partial pressure of the solvent in solution and inhibit its diffusion into the environment.

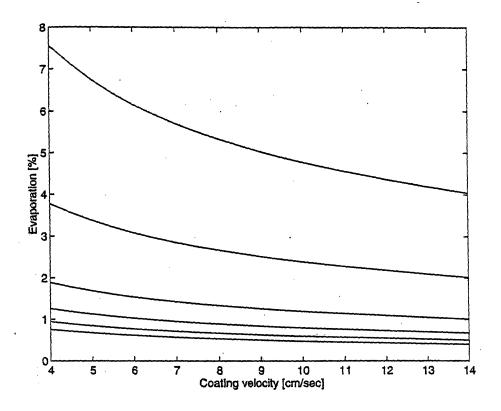


Figure 8. Total solvent evaporation at the edge of a disk after coating with wet thicknesses of 5, 10, 20, 30, 40, 50 µm (top to bottom).

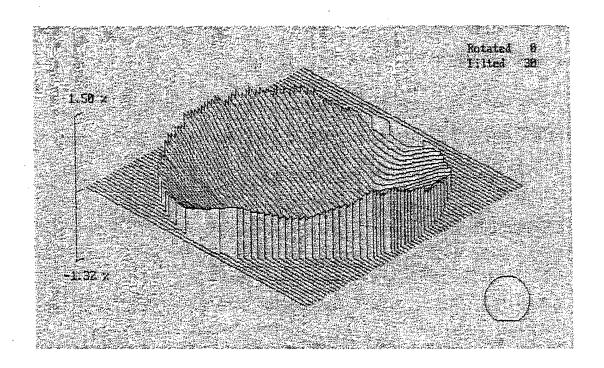


Figure 9. Map of final (dry) coating thickness.

Chapter 3

Apparatus

The apparatus consists of the extrusion spin coater used by Derksen [1], a thermometer/hygrometer, a spray bottle used to apply the solvent during static evaporation tests, and a humidity generator used to produce a higher solvent saturation level.

3.1 The Extrusion Spin Coater

The extrusion spin coater consists of 4 systems. The steps for its operation is shown in Figure 10. The systems are the spinner module, the positioning system, the photoresist dispense system, and the control system.

3.1.1 Spinner Module

The spinner module is a SVG 90SE coater module. The module has two servomotors. The first servomotor is used to spin the chuck. The second motor is used to elevate the chuck to load and unload the wafers. As shown in Figure 11, there is a catch cup at the lowest chuck position. The catch cup performs three purposes. The first purpose is to

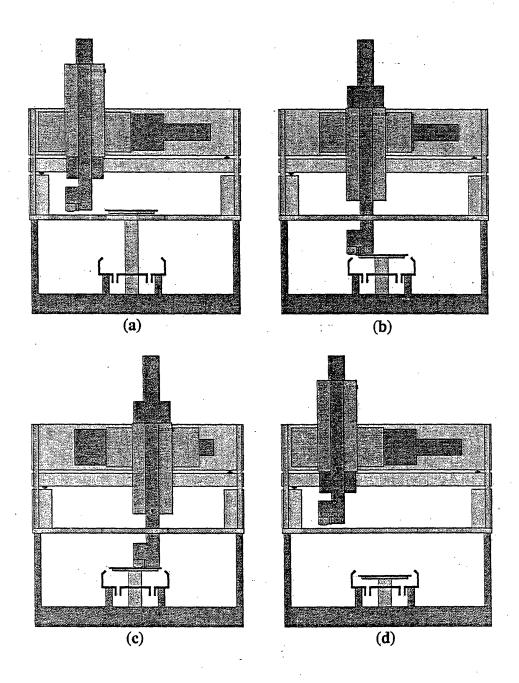


Figure 10. Extrusion-spin coating process. (a) Wafer is placed on vacuum chuck. (b) Wafer is lowered into coating position and extrusion die is positioned at the outer edge of the wafer. (c) Wafer is rotated as the extrusion die moves along the diameter of the wafer until the extrusion die completely crosses the center of the wafer. (d) Extrusion die is removed, and wafer is lowered into the catch cup and rotated at high speed.

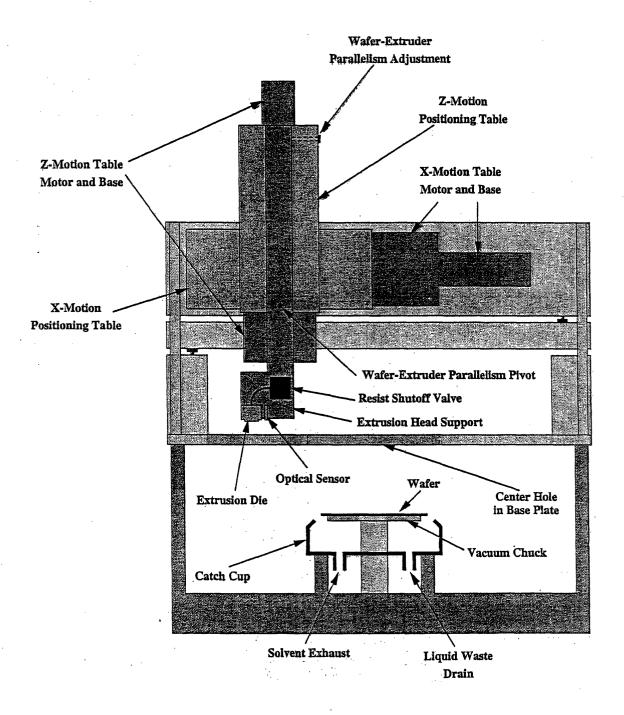


Figure 11. Front view of extrusion coater.

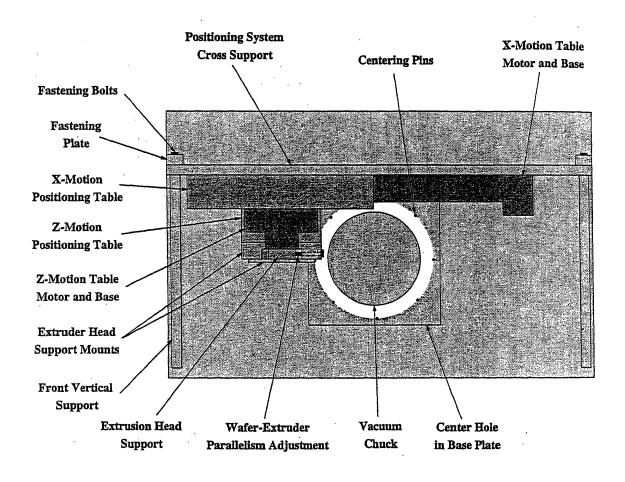


Figure 12. Top view of extrusion coater.

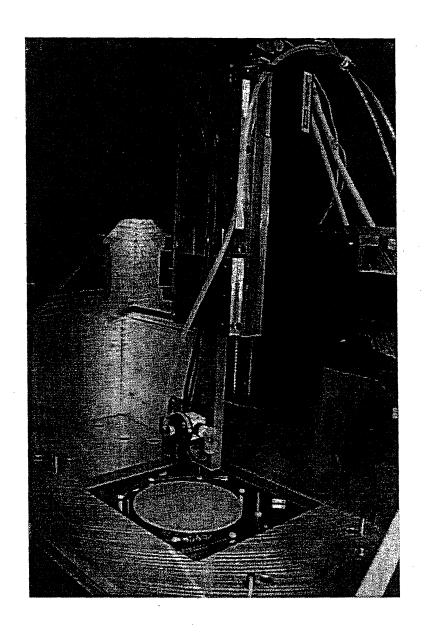


Figure 13. Photograph of extrusion coater. Scale: 1 cm = 7.25 cm.

catch and drain waste solvent into the catch bottle. The second purpose is to remove the evaporated solvent through an exhaust vent. Finally it is used to direct the flow of air over the wafer to avoid turbulence. A centering device at the top of the coater module has three vertical pins for supporting loose wafers before and after processing and Teflon pins for centering wafers on the chuck.

3.1.2 Positioning system

The two axis positioning system, shown in Figures 12 and 13, is mounted on a vertical aluminum plate above the spin coater. It consists of 2 Parker Daedal motion tables that provide 25 cm of motion driven by 5 pitch ball screws. The z-axis table is mounted on the x-axis table and the extrusion system is mounted, in turn, on the z-axis table.

3.1.3 Photoresist Dispense System

The photoresist dispense system is driven by a Millipore Gen 2 displacement pump with a Gen 2 Plus controller. The photoresist is pumped from a high-density polypropylene bottle through a T-junction. One branch feeds into the extrusion die. The other branch contains a needle valve which controls the amount of photoresist drawn from the flow to produce lower flow rates.

3.1.4 Control System

The position and spinner module is controlled by a Parker Compumotor AT6450 Controller. It has 4 servomotor controls, an analog-to-digital converter, and digital inputs and outputs. The gap distance between the extrusion head and the wafer is controlled by a Philtec RC140C optical sensor. The desired coating motion is produced by programs downloaded from a PC.

3.2 Solvent Saturation Equipment

The equipment used in addition to the extrusion spin coater are a thermometer/hygrometer, a spray bottle for solvent application, and a pump humidifier used to conduct continuous flow experiments. The AZ EBR solvent is used in these experiments.

The thermometer/hygrometer is a VWR Model 35519-048 Electronic Digital Hygrometer/Thermometer. It is capable of an accuracy of 1 °C and 2% relative humidity.

The spray bottle projects a conical spray of solvent and is used to coat the chamber above the catch cup during the static solvent evaporation tests. The quantity of solvent dispensed through the spray nozzle is irrelevant. The surfaces are coated with sufficient solvent that all surfaces remain wet during the experiment. A sheet of plastic seals the exhaust vent during experiments with no ventilation.

The pump humidifier is an air pump with a 4A motor to drive air into the base of a fluid column. As the air bubbles through the fluid column, it will become saturated with vapors from the fluid. The saturated environment is then pumped into the chamber above the catch cup.

Chapter 4

Experimental Results and Discussion

4.1 Experimental Procedure

The objective of these experiments was to examine photoresist coating uniformity with varying solvent concentrations in the environments. There were four experiments in all. The first experiment was a high dispense volume spin coating experiment. The second and third experiments were extrusion-spin coating tests with varying solvent concentrations in the environment. The last experiment was an extrusion-spin coating test conducted with a continuous feed of air with a high solvent concentration.

4.1.1 High Dispense Volume Spin Coating Experiment

There were two objectives to this experiment. The first objective was to establish a baseline to indicate the best uniformity to be attained with the spin coating module. The second objective was to examine the effect of an environment with a solvent concentration on spin coating uniformity.

Two test runs were carried out. The first test run was a plain spin coating test. A low concentration solvent environment was applied in the second test run. Spin coating

was simulated on the extrusion-spin coating apparatus by manually pouring the photoresist onto the substrate. The wafer was then spun at high speed to spread the coating and to remove the excess resist. To apply the low concentration environment, the walls of the coating chamber was coated with solvent. The solvent was then given 2 minutes to evaporate. The spin coating process was then executed. The wafers were then baked for 30 minutes to remove any remaining solvent.

For this and all subsequent experiments, the wafers were sent to the Trek Division of the Silicon Valley Group, Inc. for measurements. The mean and standard deviation data were taken using a Therma-Wave Optiprobe spectral interferometer.

4.1.2 Low Dispense Volume Extrusion-Spin Coating Experiment

The objective of this experiment was to examine the effect of a low concentration solvent environment on coating uniformity in the critical, low-dispense-volume regime. The extrusion-spin coating process is shown in Figure 9. Two extrusion spin coating test runs were carried out. The flow rate, coating time, and dispense volumes for both runs were approximately 0.016ml/sec, 29.89secs, and 0.48ml. A low concentration solvent environment was applied in the same fashion as described in the spin coating experiment.

After the high speed spinning phase, the wafers were baked for 30 minutes to remove any remaining solvent. Finally, the wafers were measured to obtain the mean thickness and the standard deviation. No spin coating runs were performed in this and subsequent

experiments because traditional spin coating methods were unable to completely cover the wafer surface at such low dispense volumes.

4.13 Uniformity Trend Experiment

The objective of this experiment was to determine the effect on the coating uniformity with increasing concentrations of solvent in the coating environment. With one exception, three sets of tests runs were made. The first set was two extrusion-spin coatings carried out without the benefit of a solvent environment. The second set was a test run made with a low concentration solvent environment. The environment was created via the method described in Section 4.1.2. In the last test run, a higher concentration solvent environment was created by sealing off the ventilation during the solvent application and the extrusion-coating phase. This resulted in a higher solvent concentration within the coating chamber. The ventilation was unsealed just prior to the high speed spinning phase to allow for proper air flow around the wafer. The wafers were then baked and measured for the coating thickness and standard deviation.

4.1.4 Dynamic Evaporation Experiment

The dynamic evaporation test differs from the static test in that the saturated environment was not created by evaporation off the chamber surface. Rather, air with a high solvent concentration was created using the pump humidifier as described in the Apparatus

section. That air was pumped into the chamber. Tests were first carried out with deionized water and solvent to determine the maximum saturation level and the time needed
to reach that level. This was followed by experiments in which first de-ionized water and
then solvent-rich environment were pumped into the chamber. The air was pumped into
the chamber to maximum saturation. The coating process was then begun. During the
coating process, the nozzle of the humidifier was directed towards the outer edge of the
wafer with the intent of retarding evaporation at the edge. Tests without a saturated
environment were carried out to provide a control.

4.2 Experimental Conditions

During all experiments, the extrusion-spin coater was in a laminar-flow hood which constantly forced filtered air downward over the extrusion-spin coater. The temperature in the room was unregulated and ranged from 19 to 27°C. The relative humidity was also unregulated, between 19 and 30%. However, these two parameters did not change within the course of each experiment.

4.2 Results

The results from the high dispense volume spin coating experiment are shown in the Figure 15. The data shown are the standard deviation from the mean thickness of the coating. The mean, standard deviation, and other pertinent data are shown in Appendix B.

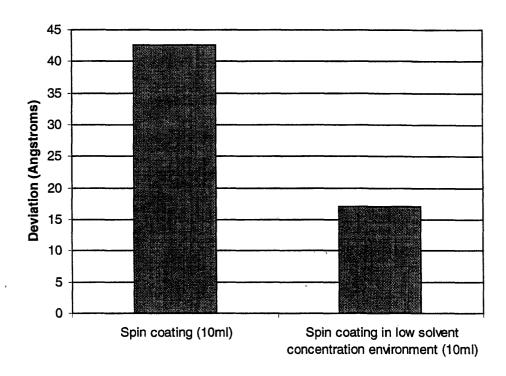


Figure 15. The high volume dispense spin coating experiment.

The spin coatings with and without a low concentration solvent environment had deviations of 42.53Å and 17.06Å respectively. The efficiency of both coatings was 1.57%.

The low dispense volume extrusion-spin coating experiment showed a large improvement in uniformity due to the application of a low concentration solvent environment. The deviation on the standard extrusion-spin coating test was 334.61Å, while the deviation on the test run with the solvent environment was only 56.16Å. The efficiency of the coatings is 32.83%.

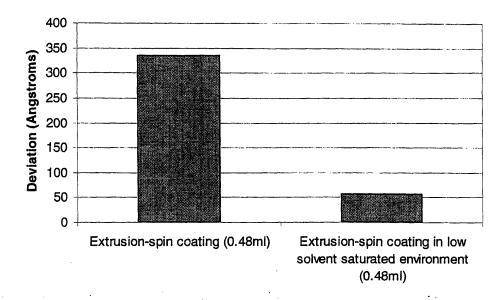


Figure 16. The low dispense volume extrusion-spin coating experiment.

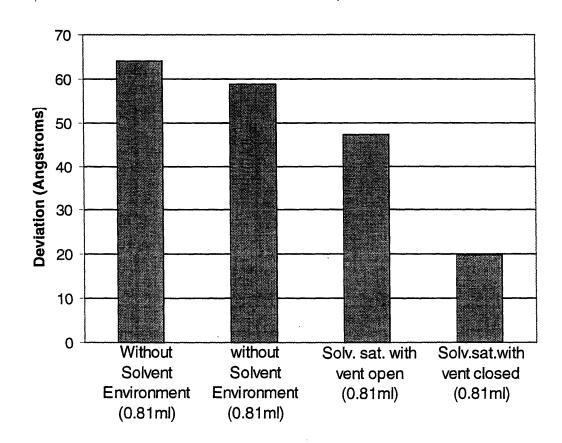


Figure 17. Uniformity trend experiment. Note that the extrusion-spin coating with a moderate solvent concentration experiment yielded a result (19.84Å) that is nearly the same as the best result in the baseline with an efficiency that is an order of magnitude better.

Table 1. The measurement of the percent change in humidity as moist air created by the pump humidifier is pumped into the coating chamber.

Time (secs)	Ventilation Open (%)	Ventilation Closed (%)	
0	20	19	
30	25	45	
60	30	56	
90	32	60	
120	37	62	
150	40	62	

The uniformity trend experiment shows that uniformity does improve with increasing concentrations of solvent in the coating environment. The standard extrusion-spin coating tests showed deviations of 64.1Å and 58.74Å respectively. The coating carried out in the low solvent concentration environment yielded a deviation of 47.28Å. The coating carried out in the moderate solvent concentration environment had a deviation of 19.84Å. The efficiency of this experiment was 19.33%.

No measurements of solvent concentration were recorded by the hygrometer. However, tests done with de-ionized water show that the increase in the humidity is usually no more than ten percent above the room humidity. The solvent, with a higher evaporation rate, can be assumed to reach a concentration not much higher than that.

The concentration levels that can be achieved by the pump humidifier are shown in Table 1. The former is with the exhaust vent open and the latter is with the exhaust vent closed.

During trial runs with de-ionized water, many particles were observed on the wafer surface. Because of the high particle count and the subsequent damage to the coatings during the high speed spin phase, the runs did not yield any usable data. No trial runs using solvent in place of the de-ionized water were carried out.

4.3 Discussion

The low dispense volume extrusion-spin coating experiments showed that a substantial improvement in uniformity can be achieved with the application of even a minor amount of solvent concentration in the coating environment. There was an improvement of nearly 280Å between the two coatings. At high dispense levels, as shown by the 10ml spin coating tests, the coating made with the solvent environment still demonstrated a noticeable improvement over the coating made by spin coating alone. This has shown that the application of a solvent environment of even modest concentrations can significantly reduce solvent evaporation during the extrusion coating phase and thus improve the wafer uniformity.

The uniformity trend experiments have shown that there is a strong trend of continued improvements in uniformity with increasing levels of solvent concentration. The low solvent concentrations that were achieved in this experiment still resulted in deviations that approached the best result obtained in the high dispense volume spin coating baseline. The best uniformity obtained in this test was 19.84Å, which was only slightly more than

the 17.06Å result obtained in the spin coating test. Moreover, the 19.33% efficiency of the extrusion-spin coating test was more than an order of magnitude greater than the 1.57% efficiency of the spin coating test. While the results still do not meet the standards required by industry, it seems that extrusion-spin coating used in conjunction with the solvent concentration environment may have the potential of meeting that requirement.

Due to the presence of large numbers of particles in the high-moisture-concentration airflow during the dynamic evaporation experiment, no usable results were available. However, the pump humidifier was able to provide humidity increases of up to 40% when tested with de-ionized water. Given that water has a lower rate of evaporation than the solvent, the estimate based on the de-ionized water is a conservative one. With a more effective particle filtering apparatus, the dynamic experiment should yield more information on the effect of a high solvent concentration environment on the coating uniformity.

There are several avenues for further research. The main one is to study the effect of high solvent concentrations on coating uniformity. The design of a pump humidifier and exhaust system that can introduce and maintain variable levels of solvent saturation would permit a more precise analysis of the effect on uniformity. Better filtering schemes have to be put into place to prevent the deposition of particles onto the wafer surface. Once the optimal range of solvent saturation has been determined, a process must be designed that maximizes the efficiency of the process while minimizing the wastage of the solvent. One of the possible avenues is to create a scheme by which the solvent

environment can be rapidly introduced and evacuated. This may include the study of other improvements mentioned by Derksen such as the use of a bead vacuum to maintain coating bead stability at higher coating speed. A higher coating speed would not only reduce the evaporation time, but would also improve the overall process time.

Chapter 5

Conclusions

This study has shown that increasing the solvent-air ratio in the atmosphere above the wafer does serve to reduce evaporation during the coating phase. This, in turn, results in an improvement in coating uniformity. At low dispense volumes of approximately 0.5 ml, substantial improvements in uniformity were achieved with low solvent concentrations. The standard deviation decreased from 335Å to 56Å. The extrusion-spin coating with the highest achievable concentration of solvent environment had a deviation of 19.84Å, only slightly higher the the high dispense volume spin coating baseline of 17Å. This was achieved with an efficiency an order of magnitude higher than that of the spin coating process. The application of a solvent saturated environment has been shown to be a viable method for improving the uniformity of photoresist coatings. Further experimentation will be necessary to determine whether uniformity results of the extrusion spin coating process can be further improved to meet industrial standards.

Appendix A

Evaporation from a Spinning Disk

Following Lienhard [7], we can calculate the mass transfer rate per unit area, m'', from:

$$m'' = g \ln(1 + B_c) \tag{A.1}$$

where g is the mass transfer coefficient at zero net mass transfer and B_s is the mass transfer driving force. (Liquid-phase resistance to solvent diffusion is neglected in this model.)

When solvent is the only species transferred (i.e. no air diffuses into the solvent):

$$B_s = \frac{m_{s,\varepsilon} - m_{s,s}}{m_{s,s} - 1} \tag{A.2}$$

where $m_{s,s}$ is the mass fraction of solvent in the air far away from the fluid surface and the $m_{s,s}$ is the mass fraction of solvent in the air just above the fluid surface. If we assume that any evaporated solvent gets carried away quickly, then $m_{s,s} = 0$. If we assume that there is pure solvent at the liquid surface, we can find $m_{s,s}$ from the saturation pressure of the

solvent. We can find the properties of the air-solvent mixture by using the procedure detailed by Lienhard.

The mass transfer coefficient, g, can be found by using an analogy between convective heat transfer and mass transfer which is only valid for low mass transfer rates.

The heat transfer from a rotating disk is a laminar flow can be found from [2]:

$$Nu_r = \frac{0.585 \,\mathrm{Re}^{1/2}}{0.6/\,\mathrm{Pr} + 0.95/\,\mathrm{Pr}^{1/2}} \tag{A.3}$$

where Nu_r is the Nusselt number, Pr is the Prandtl number, and Re is the Reynolds number:

$$Re = \frac{\Omega r^2}{v} \tag{A.4}$$

The transition to turbulence (when Equation A.3 becomes invalid) begins at $Re_{tr} = 2.4 \times 10^5$.

Using this analogy, we can replace the Nusselt number and Prandtl number with the Sherwood number and the Schmidt number [9]:

$$Sh_r = \frac{gr}{D_{as}\rho} = \frac{0.585 \text{Re}^{1/2}}{0.6/Sc + 0.95/Sc^{1/3}}$$
 (for any Sc)

where $Sc = v/D_{as}$, D_{as} is the diffusivity between air and the solvent on th disk surface, and g is the mass transfer coefficient. Solving for the mass transfer coefficient yields:

$$g = \frac{0.585 D_{as} \rho}{0.6 / Sc + 0.95 / Sc^{1/3}} \left(\frac{\Omega}{v}\right)^{1/2}$$
(A.5)

This result is very similar to that of Kreith et al. [6].

The air-solvent diffusion coefficient can be estimated using the Kinetic Theory of Gases by the methods of Chapman and Enskog [12].

Appendix B

Experimental Data

Table B1. High dispense volume spin coating for use as a baseline. Even at high volumes, the presence of a solvent environment produces improvements in uniformity.

Test Runs	Dispense Volume (ml)	Efficiency (%)	Mean (Angstroms)	Deviation (Angstroms)
Spin Coating	10	1.57	7379.92	42.53
Spin Coating with low solvent environment	10	1.57	7703.90	17.06

Table B2. Low dispense volume extrusion spin coating. The presence of a low solvent concentration environment results in a dramatic change in uniformity.

Test Runs	Dispense Volume (ml)	Efficiency (%)	Mean (Angstroms)	Deviation (Angstroms)
Extrusion Spin Coating	0.48	32.83	7117.33	334.61
Extrusion Spin Coating in low solvent environment	0.48	32.83	7368.02	56.16

Table B3. Experiment determining the trend in uniformity of the extrusion spin coating as a result of varying solvent concentrations in the environment.

Test Runs	Dispense Volume (ml)	Efficiency (%)	Mean (Angstroms)	Deviation (Angstroms)
Extrusion Spin Coating, no solvent environment	0.81	19.33	7849.54	64.10
Extrusion Spin Coating, no solvent environment	0.81	19.33	8026.09	58.74
Low solvent concentration environment	0.81	19.33	7774.92	47.28
Moderate solvent concentration environment	0.81	19.33	7773.69	19.84

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