2006

Process characterization of thick photoresist for the thin film head industry

Clarence Hsieh
San Jose State University

Follow this and additional works at: https://scholarworks.sjsu.edu/etd_theses

Recommended Citation

Hsieh, Clarence, "Process characterization of thick photoresist for the thin film head industry" (2006).
Master's Theses. 3003.
DOI: <https://doi.org/10.31979/etd.jcy3-39qt>
https://scholarworks.sjsu.edu/etd_theses/3003

This Thesis is brought to you for free and open access by the Master's Theses and Graduate Research at SJSU ScholarWorks. It has been accepted for inclusion in Master's Theses by an authorized administrator of SJSU ScholarWorks. For more information, please contact scholarworks@sjsu.edu.

PROCESS CHARACTERIZATION OF THICK PHOTORESIST FOR THE THIN
FILM HEAD INDUSTRY

A Thesis

Presented to

The Faculty of the Department of
Chemical and Materials Engineering
San Jose State University

In Partial Fulfillment
of the Requirements for the Degree
Master of Science

by

Clarence Hsieh

December 2006

UMI Number: 1441097

INFORMATION TO USERS

The quality of this reproduction is dependent upon the quality of the copy submitted. Broken or indistinct print, colored or poor quality illustrations and photographs, print bleed-through, substandard margins, and improper alignment can adversely affect reproduction.

In the unlikely event that the author did not send a complete manuscript and there are missing pages, these will be noted. Also, if unauthorized copyright material had to be removed, a note will indicate the deletion.

UMI[®]

UMI Microform 1441097

Copyright 2007 by ProQuest Information and Learning Company.

All rights reserved. This microform edition is protected against unauthorized copying under Title 17, United States Code.

ProQuest Information and Learning Company
300 North Zeeb Road
P.O. Box 1346
Ann Arbor, MI 48106-1346

© 2006

Clarence Hsieh

ALL RIGHTS RESERVED

**APPROVED FOR THE DEPARTMENT OF CHEMICAL
AND MATERIALS ENGINEERING**

9/13/06
Dr. Gregory L. Young

Dr. Melanie McNeil

Dr. Prabodh Ratnaparkhi (Hitachi GST)

APPROVED FOR THE UNIVERSITY

11/02/06

ABSTRACT

PROCESS CHARACTERIZATION OF THICK PHOTORESIST FOR THE THIN FILM HEAD INDUSTRY

By Clarence Hsieh

Thin film head (TFH) has been the dominant manufacturing process in the disk drive industry for the past 30 years. The manufacturing process involves many thin magnetic and non-magnetic layers ranging from 0.5 to 10 μm . However, there is still a need for a thick process layer up to 40 μm for the copper electrical contacts. With the recent advancement in MEMS, thick photoresist for contact aligners is now available for TFH processing.

This thesis characterized a thick photoresist using a reduction stepper. In addition to coating and exposure parameters, time between coating and expose was found to be an important factor for process control. The final process defined by the DOE produced straight electroplated features that compared favorably to the contact aligner process.

TABLE OF CONTENTS

CHAPTER ONE INTRODUCTION	1
CHAPTER TWO LITERATURE REVIEW	5
2.1 Exposure Tools	5
2.2 Materials	9
2.2.1 Resist Development	11
2.2.2 Resist Tone.....	12
2.3 Effect of Coating and Bake Conditions	15
2.4 Effect of Expose Condition.....	17
2.5 Effect of Development.....	18
2.6 Process Characterization.....	19
2.7 Summary	21
CHAPTER THREE HYPOTHESIS AND OBJECTIVES.....	22
3.1 Hypothesis.....	22
3.2 Objective	22
3.3 Justification.....	23
CHAPTER FOUR EXPERIMENTAL METHODS.....	24
4.1 Overview of Experiment.....	24
4.2 Materials	25
4.3 Screening Tests	26
4.3.1 Coat.....	28
4.3.2 Expose.....	28

4.3.3	Develop	29
4.3.4	Process Compatibility	30
4.4	Photo Matrix	30
4.5	Design of Experiment	32
4.6	Verification	35
CHAPTER FIVE RESULTS		36
5.1	Material Screening	36
5.2	Focus Effect	39
5.3	DOE Results.....	40
5.3.1	Coater 1 Results	41
5.3.2	Coater 2 Results	43
5.3.3	Coater Selection	45
5.4	Model Verification.....	46
CHAPTER SIX CONCLUSIONS		48
CHAPTER SEVEN FUTURE WORK		49
REFERENCES.....		50

LIST OF FIGURES

Figure 1. Through-mask electroplating.....	3
Figure 2. Consequences of a 0.1 μm alignment error (upper line pair) and a 0.1 mrad die rotation (lower pair line) on the final 0.5 μm wide pattern.....	8
Figure 3. Comparison of aerial images at the resist top for (perfect) contact, proximity, and projection printing.....	9
Figure 4. UV exposure transforms the insoluble component of the positive photoresist into soluble products.....	10
Figure 5. Photochemical reaction scheme of diazonaphthoquinone (DNQ) Novolak-based positive resist.	12
Figure 6. Negative photoresist reaction. KTFR (free-radical-initiated photocross-linking). X = aliphatic or aromatic group.	12
Figure 7. Process comparison between positive and negative photoresist.	13
Figure 8. Comparison between regular resist and CAR where Φ is the quantum efficiency.....	14
Figure 9. Typical swing curve.	16
Figure 10. Typical Bossung plot.....	19
Figure 11. Overview of experimental procedure.	25
Figure 12. Exposure matrix.....	29
Figure 13. Focus matrix and feature size sampling plan.	31
Figure 14. Optical measurement of via.....	31
Figure 15. Measurement sampling plan.....	33

Figure 16. Full factorial DOE.	35
Figure 17. SEM images of electroplated via structures using negative photoresist C.....	37
Figure 18. SEM images of electroplated via structures using negative photoresist C after oxygen RIE.	38
Figure 19. SEM image of negative photoresist C residual between electroplated via structures after photoresist stripping.....	38
Figure 20. SEM image of electroplated via structure using positive photoresist A.	39
Figure 21. Focus matrix result.	40
Figure 22. DOE prediction using Coater 1.	42
Figure 23. DOE prediction using coater 2.	44
Figure 24. SEM images of electroplated via structures using process conditions for Coater 2.....	47
Figure 25. SEM images of electroplated via structures using contact aligner.....	47

LIST OF TABLES

Table 1. Photoresist Category.	26
Table 2. Photoresist Screening Criteria.	27
Table 3. Screening Results.....	36
Table 4. Parameter Range for the DOE.	41
Table 5. Summary of Recommended Process Conditions from the DOE.....	45

CHAPTER ONE

INTRODUCTION

Computer disk storage system was first introduced by IBM in 1956. In 1979, IBM shipped the first thin film head disk drive [1]. In the heart of the disk drive is the magnetic thin film head (TFH) that reads and writes magnetic data from and onto the magnetic disk. TFH is constructed like a horseshoe magnet and consists of three main components: the magnetic core made out of high moment materials like nickel-iron alloys, coils made out of copper, and a gap made out of alumina. Writing of data is done by the tips of the magnetic core with magnetic flux generated by currents flowing through the coils. The magnetic flux passes through the alumina gap and magnetizes the magnetic disk. Reading of data is done by sensing the transitions in the magnetic flux of the disk [2].

The manufacturing of TFH involves both dry and wet processes for the various thin film layers. The main magnetic sensor, as well as some of the insulating layers, is fabricated utilizing dry processes. Thin layers of materials are vacuum deposited onto the substrate and then patterned by photolithography and etched either with reactive ion etch or with an ion beam to define the desired structures. The rest of the layers are fabricated using wet processes where electroplating is the main processing technique. First, a thin metal layer is vacuum deposited onto the substrate as the seed layer. Structures are then defined by photolithography and the substrate is placed into a chemical bath for electroplating. Whereas the dry process is the preferred method to deposit thin layers

because of the precision, wet process is the preferred way to electrodeposit thick metal layers of nickel-iron alloys, copper and gold, because of the rate of deposition.

There are several advantages for electroplating as a process for metal deposition as compared to vacuum deposition. Electroplated films have high rates of deposition. Plating cells are relatively inexpensive as compared to vacuum deposition systems.

Small plated features are easier to be defined and controlled because the patterns are defined by photolithography. Although photolithographic patterns are also used in the dry process for feature definition, there is a lack of methods for selective materials etching [1].

Most of the photolithography layers in the TFH manufacturing process involve thin photoresist up to about 10 μm . However, there is still a need for thick photoresist up to 40 μm . In one of the final steps in the TFH manufacturing process, electrical contacts to the device are made by electroplating 40 μm of copper into vias. The process involves applying the thick photoresist on top of a copper seed layer and then patterned into vias. Copper is then electroplated by through-mask plating as in Figure 1. After electroplating, the thick photoresist will be removed leaving pillars of electroplated copper as electrical contacts.

Figure 1. Through-mask electroplating.

Without the use of thick photoresist, there are two processing methods to form these copper electrical contacts. The first is to use just a single layer of 10 μm photoresist. After the photoresist is imaged with the via patterns, the wafer is electroplated to 40 μm . The resulting copper features look like a big mushroom because of overplating. This process only works for electrical contacts that are designed to be far apart. As the distance of the electrical contacts become closer, there is no more room for overplating.

The second method is to perform multiple coating to achieve the desired photoresist thickness. However, this method is very costly in manufacturing due to the time involved in multiple coat and bake steps. Furthermore, the lower layers in the multiple coating scheme will get baked longer than the top layers resulting in a

photosensitivity gradient within the photoresist stack. Dimensional control throughout the photoresist film becomes a challenge.

The processing methods for thin and thick photoresist are quite different and present different challenges. Whereas resolution is the biggest challenge for thin photoresist process, wall profile is the biggest challenge for thick photoresist process. It is best in manufacturing to match exposure tools with different types of photoresist to achieve optimal process control. When this is not feasible due to the limitations of the existing manufacturing tools, process characterization with existing tools becomes necessary to define new process conditions. For thick film photolithography process, parameters that need to be explored are types of photoresist, types of exposure tool, bake temperature of the photoresist, exposure energy, exposure focus offset, and the developer types and time. Together, all these factors will define the process window.

This research is significant because it enables TFH processing to maintain on the technology roadmap for overall footprint reduction. Without a thick photoresist process, the device footprint is mostly defined by the size and separation of the electroplated copper features. However, a thick photoresist process will offer better dimensional control of the vias and thus allows the electroplated copper features be designed closer to each other in a reduced device footprint for new generation products.

CHAPTER TWO LITERATURE REVIEW

Photolithography has been an integral part of semiconductor manufacturing since 1960 [3]. As the industry trend goes towards smaller and smaller critical feature sizes, major advances in technology both in materials and equipment are required to keep up.

2.1 Exposure Tools

The early lithography technology was limited by the 1X contact aligner. These tools were problematic because of the wear and tear of the masks. Frequent cleaning of the masks was required to remove the contamination on the masks. These masks were also damaged due to frequent handling.

In order to reduce the mask contamination issue, 1X proximity and 1X projection aligners were introduced. These tools were able to achieve resolutions on the order of 2-3 microns. As the wafer size got larger and larger, 1X tools were no longer sufficient. The amount of overlay errors caused mainly by wafer distortion did not meet the industry requirements. New exposure tools had to be developed.

Several attempts were made to manufacture wafer steppers in the 1970s. Finally, GCA corporation introduced the first commercial wafer stepper in 1977 [3]. The use of the wafer stepper enabled printing on larger wafers without the cost of having expensive

and big projection lens. Since the mask location inside the wafer stepper was further away from the wafer surface, the mask contamination issue was also eliminated. The introduction of wafer stepper marked the beginning of the advances in photolithographic equipment.

The reduction stepper was introduced after the 1X wafer stepper to solve the problem of the shrinking feature sizes. Before the reduction stepper, the feature sizes on the mask and the printed features on the wafer were approximately the same. As the features got smaller, it was increasingly difficult for mask manufacturers to make the masks. With the reduction stepper, the mask features could be made a number of factors larger than the wafer features. For example, a 5 μm mask feature would result into an approximately 1 μm feature on the wafer with a 5X reduction stepper. Not only was there a relief in the mask feature size, the reduction stepper also improved the mask-induced errors on the wafer. If the tolerance of the mask feature were 0.5 μm , the equivalent tolerance on the wafer level would be reduced 0.1 μm .

As the technology progresses, more and more advance photolithographic systems become available that utilize shorter and shorter wavelengths of light to define smaller and smaller features [4]. The direct proportional relationship between resolution and exposure wavelength is described by the Raleigh equation in Equation 1.

$$R = k_1 * \frac{\lambda}{NA}$$

Equation 1

where R = resolution

k_1 = process constant

λ = wavelength of exposure tool

$NA = n \sin \theta$ = numerical aperture

θ = the half-angle of the maximum cone of light that can enter or exit the lens

The complexity of the lithographic lens also increased with each generation of tools. These advance systems include 248 nm steppers, 193 nm scanners, EUV, and x-ray lithography.

The advancement to print smaller features was not without penalty. Features that used to be completely defined by the mask for the contact aligner had to be broken up into smaller fragments and stitched together for the advance reduction systems as in Figure 2. The concern with the induced overlay errors prompted new development in the alignment systems by stepper manufacturers for their advance systems.

Figure 2. Consequences of a $0.1\ \mu\text{m}$ alignment error (upper line pair) and a $0.1\ \text{mrad}$ die rotation (lower pair line) on the final $0.5\ \mu\text{m}$ wide pattern.

The second penalty was that only features of limited complexity could be printed with most of the steppers. There was a limited amount of images that could be placed on each reticle and different steppers could only accommodate a fixed number of reticles [5].

The last penalty was the decrease in image quality from the advance systems as described in Figure 3. Contact aligner resulted in the best aerial image through a mask. As the mask distance increased further away from the wafer surface, from proximity to projection, the aerial image became more distorted. The only way to improve the aerial image and replicate the mask features onto the wafer surface exactly was through resist chemistry. With the use of a reduction stepper in this study, the stepper related limitations would define the thick photoresist process parameters.

Figure 3. Comparison of aerial images at the resist top for (perfect) contact, proximity, and projection printing.

2.2 Materials

Photoresist by definition must have two components in its formulation. One is to be photosensitive and the other is to be resistant to etching. When the photoresist gets exposed to light, it undergoes a chemical transformation that makes it either go from insoluble to soluble or from soluble to insoluble. The difference in solubility between the exposed and unexposed photoresist then forms into features as in Figure 4.

Most of the photoresist used in the TFH industry ranges from 1 μm to 10 μm [6]. It is not until recently that thick resist has become available due to the increasing growth

in the electro-mechanical systems (MEMS) industry [7 and 8]. These new materials have been used in applications of more than 1000 μm [8 and 9].

Figure 4. UV exposure transforms the insoluble component of the positive photoresist into soluble products.

2.2.1 Resist Development

In the early development of positive photoresist, the change in solubility was achieved by cross-linking. As the molecular weight of the polymer increased due to cross-linking, its solubility decreased. However, this led to swelling as well as adhesion failures. It was not until 1930s that Oskar Süss discovered diazoquinine novolac resists (DNQ). When exposed to light, DNQ rearranged to form carboxylic acid and released nitrogen as in Figure 5 [10]. This also transformed the base insoluble sensitizer into base soluble photoproduct. Since the reaction to light was a chemical rearrangement reaction instead of a cross-linking reaction, the boundaries between the soluble and insoluble were well defined. The transformation mechanism from soluble to insoluble for negative tone photoresist was different as indicated by Figure 6 [11]. The photosensitive components in the negative photoresist crosslinked upon ultraviolet exposure and changed from soluble to insoluble in the development solution.

Resist development is an ongoing field. New photoresist materials such as bioresist, imprint photoresist, and strippable negative photoresist are still being developed for the various industries [12, 13, and 14].

Figure 5. Photochemical reaction scheme of diazonaphthoquinone (DNQ) Novolak-based positive resist.

Figure 6. Negative photoresist reaction. KTFR (free-radical-initiated photocross-linking). X = aliphatic or aromatic group.

2.2.2 Resist Tone

Positive tone DNQ photoresist is widely used in the TFH industry. In positive photoresist, the exposed areas become base soluble and could be developed in a hydroxide solution such as potassium hydroxide (KOH) or tetra-methyl ammonium hydroxide (TMAH) as shown in Figure 7.

Although negative tone photoresist is also available for the TFH industry, it is not commonly used because historically negative photoresist is very hard to remove. Most of the use of photoresist in TFH is only to form temporary features and be removed once the permanent features are formed either by electroplating, etch, or liftoff processes. Furthermore, in the case of SU-8 made by MicroChem Corporation, the photoresist developer is an organic solvent that is not environmentally friendly [14].

Figure 7. Process comparison between positive and negative photoresist.

One other category in photoresist is the chemically amplified resist (CAR). The reason for inventing CAR was to make use of fewer photons in the photochemical

reaction. This was necessary because advance light sources utilized shorter exposure wavelengths that generated fewer photons.

Figure 8. Comparison between regular resist and CAR where Φ is the quantum efficiency.

Unlike the DNQ photoresist that has a photoactive compound (PAC), CAR has a photoacid generator (PAG). Instead of having the photons reaching deep into the DNQ photoresist to complete the photochemical reaction, CAR only needs enough photons to initiate the photochemical reaction that generates photoacid. Once this catalytic reaction is started, it will continue in the presence of heat as shown in Figure 8.

2.3 Effect of Coating and Bake Conditions

Coating conditions directly affects the thickness of the photoresist. The spin coating film thickness can be expressed as in Equation 2 where thickness is inversely proportional to the spin speed.

$$d \propto \frac{1}{\sqrt{\omega}} \quad \text{Equation 2}$$

where d = film thickness

ω = spin speed

The thickness control is important because the absorption or reflectance behavior of the photoresist is a non-linear function with film thickness [6, 15]. It is therefore very important in process characterization to select the optimum spin condition. A typical swing curve is shown in Figure 9. It is necessary to operate at either the peaks or the valleys of the swing curve to minimize the thin film interference effect on coating thickness. Setting up photolithography processes at these operating points will allow small variations in photoresist thickness while not affecting CD. This will improve the within wafer CD variation. If a process is setup at the steep slope regions of the swing curve, small variations in photoresist thickness can result in big variations in CD. Since the amplitude and periodicity of the swing increases with decreasing exposure wavelength, coating thickness control becomes increasingly important because the trend in the industry is to utilize shorter exposure wavelength to achieve smaller features [3, 4,

and 9]. Factors that affect the coating performance include relative humidity, photoresist and air temperature, chuck temperature, spin speed, and exhaust pressure.

Once the photoresist is applied on the wafer, the next process step is post apply bake (PAB). PAB removes excess solvents from the photoresist and allow the polymer chain within the photoresist to relax and form into ordered matrix. The temperature at which PAB occurs governs the evaporation rate of the solvent following the Arrhenius behavior [16]. PAB can be achieved by means of oven bake, hotplate bake, as well as infrared radiation [8].

Figure 9. Typical swing curve.

Besides PAB, post exposure bake (PEB) is also an important process in photolithography. PEB has different functionality on different photoresists. For CAR, PEB is necessary to propagate the photoacid generation within the exposed areas. For DNQ, not only can PEB enhance the sensitivity and process latitude, it can also reduce the standing wave effect.

Standing wave is the result when incoming and outgoing light waves interfere with each in the photoresist. PEB promotes diffusion within the photoresist thus diminishing the standing waves.

2.4 Effect of Expose Condition

Photoresist feature size is a direct function of exposure dose. Increasing exposure dose will result in a larger via size for a positive photoresist. At the optimum focus, the photoresist profile has the highest sidewall angle. Any deviation from the optimum focus both into air and into the photoresist will result in loss of sidewall angle and create photoresist foot.

Exposure latitude (EL) is defined as the exposure dose range while maintaining 10% of the nominal line width. The best EL is achieved at the optimum focus and any deviation from that process point will decrease the EL. Besides exposure dose and focus, advance steppers and scanners offer variable numerical aperture (NA) as well as partial coherence (σ) to enhance the image quality [17, 18, 19, and 20].

NA is the maximum angle of light that exits the stepper lens. σ is the ratio of the diameters of the illumination optics exit pupil to the imaging optics entrance pupil. σ value ranges from 0 for full coherent light to 1 for fully incoherent light.

2.5 Effect of Development

There are two common groups of developers used in the TFH. One is buffered metal-ion containing and the other is metal-ion free (MIF). The choice of developer is mostly governed by the type of photoresist used. One of the concerns of using metal-ion containing developer is the metal-ion contamination. However, this concern can be contained with an adequate water rinse and a careful monitoring of the ionic conductivity of the rinse water.

Development can be achieved by a number of methods such as dipping development, step puddle development, vibration development, and the reverse development. In the case of thick photoresist, Sensu et al [10] showed that step puddle development yielded the best photoresist profile after development. It was theorized that the released nitrogen molecules from within the photoresist attached themselves to the photoresist surface and form an inhibition layer. Step puddle development was the most efficient in removing this inhibition layer and thus allowed good contact between the developer and the photoresist. The other advantage of using the step puddle development was the supply of fresh developer with each puddle because the activity of the developer decreased as the concentration of dissolved photoresist increased.

2.6 Process Characterization

The two main parameters that define a photolithographic feature are exposure dose and focus. Because of the swing curve effect, a focus exposure matrix (FEM) is usually performed to define the process latitude [15, 17, 18, 19, 21, and 22]. With the FEM, a set of Bossung curves can be generated as shown in Figure 10. Each line of the Bossung curve represents one exposure dose as it goes from one end of the focus window to the other. The curvature of the plot indicates the CD sensitivity to focus. High curvature lines represent small focus window with respect to CD while flat lines represent big focus window with respect to CD.

Figure 10. Typical Bossung plot.

One other feature of the Bossung curve is that there should be a change in curvature with the plotted focus range. The focus at which the curve changes curvature is the best focus of the process. If there is no inflection point, the examined focus range is not wide enough and the best focus cannot be determined.

A Bossung plot can therefore help define a robust process where the CD does not deviate much with changing exposure dose and process focus. The best process is represented by the Bossung curve that is almost flat. In Figure 10 the flat curve is at CD=425 nm. Since the mask feature sizes are known, Bossung curve can also determine the print bias between the mask and the printed features. Given a certain CD tolerance, for example $\pm 10\%$, the process latitude is defined as a box on the Bossung plot that encapsulates the maximum CD and focus variations while having the least exposure dose variation. Figure 10 does not have a big processing window because within the exposure range, CD is quite sensitive to focus. This may also indicate that the print bias is incorrect. A new set of Bossung curves can be generated with a different range of exposure energy to find the best processing condition.

When processing thick photoresist, just the Bossung plot itself is not enough to define the process latitude. The additional parameter to investigate is the sidewall angle of the photoresist profile. Depending on the process requirement on sidewall angle, a focus offset will be applied at expose [13, 24, and 25].

2.7 Summary

Much effort has been given to lower the resolution limits with advanced lithographic systems. These advance systems are mainly used in conjunction with thin photoresist in the order of a few microns. New industries such as MEMs have prompted the development of thick photoresists utilizing contact aligners because of their wide focus range. However, these developments were mainly conducted separately without combining the use of advance lithographic system with thick photoresist. The objective of this study is therefore to characterize a new thick photoresist process for the TFH industry utilizing a reduction stepper in a manufacturing environment.

CHAPTER THREE

HYPOTHESIS AND OBJECTIVES

3.1 Hypothesis

The hypothesis of this thesis is that newly developed thick photoresists for the TFH industry should enable printing of straight vias suitable for 40 μm copper electroplating as electrical contacts. The new materials were designed for a contact/proximity aligner but should also work for a reduction stepper.

3.2 Objective

This main objective of this study was to characterize the performance of a thick photoresist in terms of sidewall profile of electroplated copper vias for a reduction stepper. The effects of process parameters such as spin coating, exposure energy, developer and sit-time were studied in order to meet the main objective. The defined thick photoresist process should provide the process control necessary for new generation products with smaller form-factor. The goal was to achieve the straightest wall with the lowest CD variation across the wafer. The results were then compared to results obtained from a contact/proximity aligner.

3.3 Justification

TFH has been using thin photoresist in manufacturing because thick photoresist was not available. In order to achieve the proper thickness, multiple apply and bake steps in conjunction with overplating had to be utilized resulting in higher manufacturing cost and poor process control. The results of this study are valuable in assessing the possible use of thick positive photoresist for TFH to simplify thick layer processing, reduce manufacturing cost, and have better process control with no overplating for future products.

CHAPTER FOUR EXPERIMENTAL METHODS

4.1 Overview of Experiment

The study began with a screening experiment of photoresists from different vendors. Screening tests were performed on 5-inch ceramic wafers deposited with a thin layer of copper. Copper was selected as the background for all photolithographic tests because the thick photoresist process was designated for the electroplating of copper. One photoresist was selected based on the screening results and continued with further characterization and verification as in the flowchart in Figure 11.

Focus expose matrix (FEM) in the form of a design of experiment (DOE) was performed to determine the best process condition for the chosen thick photoresist. The process parameters explored were exposure, focus, developer, as well as coating machines. Measurements of vias were made using optical metrology across the wafer to determine the straightness of the wall profile as well as the within wafer variation of the via dimension.

Figure 11. Overview of experimental procedure.

4.2 Materials

Two positive and two negative photoresists were selected for this study. The selection was based on the availability of single coat 50 μm photoresists for TFH from different vendors. FSI coaters were used to apply as well as bake the photoresists. I-line reduction stepper was used for all exposure tests and N-Methyl-2-Pyrrolidone (NMP) was used to remove the photoresists after electroplating.

4.3 Screening Tests

The thick photoresist characterization began with material selection from four different photoresists. The selection was based on performance and ease of process.

These photoresists included both positive and negative tone as listed in Table 1.

Table 1. Photoresist Category.

Photoresist	Tone	Specific Gravity	Nominal Thickness
A	Positive	1.07	50 μm
B	Positive	1.02-1.10	50 μm
C	Negative	1.10	50 μm
D	Negative	1.10-1.30	50 μm

Before the start of the screening process, material safety data sheets (MSDS) for all the photoresists were examined to ensure that all the chemicals were environmentally safe. A photoresist would be eliminated from consideration if it did not meet the environmental requirement. The main screening process parameters were the nominal coating conditions, exposure settings, and develop conditions recommended by the photoresist vendors listed in Table 2. In addition to the photolithographic processes, process compatibility with electroplating as well as photoresist removal was also explored in order to select one photoresist for further study. Five wafers for each of the four photoresist were used for the coating screen for a total of 20 wafers. The results from each screening test would be ranked in order to determine the best material. If all four photoresists passed the coating screen, five more wafers for each photoresist would

be used for the exposure screen for a total of another 20 wafers. However, if any of the photoresist failed the coating screen, that photoresist would be eliminated from consideration and further screening would only be performed on the remaining photoresists. At the end of the screening test, ranking was performed to select one material for further study.

Table 2. Photoresist Screening Criteria.

Process	Parameter	Criteria	Materials
Environmental	Chemical Review	Comply with company EH&S regulations	MSDS
Coat	Thickness	Single layer coating to 50 μm	5 wafers/resist
	Cleanliness	"Cotton Candy" free	
Expose	Dose to clear (positive)	<1500 mJ/cm^2	5 wafers/resist
	Dose to stay (negative)		
Develop	Time	<10 minutes	5 wafers/resist
Compatability	Photo	Use of reduction stepper	5 wafers/resist
	Electroplating	No photoresist lifting and underplating during electroplating	
	Removal	No residual photoresist	

4.3.1 Coat

Even though photoresist was applied manually during the screening experiment, coating condition was still important because the thickness and viscosity of the photoresists may present problems during the automated spin coating application in manufacturing. The feed lines to the coater may have to be altered to accommodate more viscous photoresists. The spin coating behavior of the photoresists had to be monitored to minimize the “cotton candy” effect as well as edge bead formation. This was a qualitative assessment.

4.3.2 Expose

The main exposure limitation with the use of a reduction stepper in this study was the maximum exposure energy output. Since most of the TFH processes only required exposure energies of less than 1500 mJ/cm^2 , there was an unknown consequence on increasing the exposure energy beyond 1700 mJ/cm^2 . One catastrophic consequence may be the irreversible damage of the reduction stepper optics. For this reason, the dose to clear for $50 \text{ }\mu\text{m}$ photoresists had to be less than 1500 mJ/cm^2 . The photoresist with the lowest dose to clear would be ranked the highest.

Exposure matrix was performed on all test wafers using an 8X8 array with an energy step size of 25 mJ/cm^2 starting at 500 mJ/cm^2 as in Figure 12. This covered a total range of exposure energy from 500 mJ/cm^2 to 2075 mJ/cm^2 .

500	700	900	1100	1300	1500	1700	1900
525	725	925	1125	1325	1525	1725	1925
550	750	950	1150	1350	1550	1750	1950
575	775	975	1175	1375	1575	1775	1975
600	800	1000	1200	1400	1600	1800	2000
625	825	1025	1225	1425	1625	1825	2025
650	850	1050	1250	1450	1650	1850	2050
675	875	1075	1275	1475	1675	1875	2075

Figure 12. Exposure matrix.

4.3.3 Develop

Two different developer solutions were used in this study. TMAH and KOH were both tested during the screening test to determine the proper develop times for the thick photoresists. The desired develop time was less than 10 minutes for manufacturing. The choice of which developer to use was determined by the recommendation from the photoresist vendor. KOH was used for the positive photoresist and TMAH was used for the negative photoresist. The photoresist with the shortest develop time would be ranked the highest.

4.3.4 Process Compatibility

The final screening test was process compatibility. Photolithography was only one part of this study. For the thick photoresist process to work in manufacturing, it has to be compatible with down stream processes such as electroplating and photoresist stripping. A photoresist that has great imaging qualities but poor adhesion during electroplating could not be used. Similarly, a photoresist that could not be stripped after electroplating could not be used. The screening wafers that passed the first three screening tests were electroplated with 35 μm of copper and then stripped in NMP. The photoresist that showed no sign of underplating as well as stripped cleanly with NMP would be ranked the highest.

The highest ranking photoresist would then be used for the next phase of characterization. A photo matrix would determine the best processing condition for the DOE.

4.4 Photo Matrix

With a set coating condition, a photo matrix was performed to define the best stepper condition to achieve the straightest sidewall profile. Before the start of the photo matrix, the reduction stepper capability was examined to ensure that it could accommodate thick photoresist. For the best wall profile, it was best to set the focus offset as deep into the photoresist as possible. The stepper focus for most of the TFH processes was less than 2 μm because of the use of thin photoresist. For the thick

photoresist, a focus test in Figure 13 was performed to determine if the reduction stepper was capable to operate at its maximum focus of $-50\text{ }\mu\text{m}$.

Figure 13. Focus matrix and feature size sampling plan.

Figure 14. Optical measurement of via.

The focus matrix would determine the best focus for the thick photoresist process. 10 measurements per focus cell were taken as in Figure 13. Measurements of the dark band around the vias (Xo-Xi and Yo-Yi) as in Figure 14 represented the curvature of the vias through the thick photoresist. The smallest dark band represented the straightest sidewall and the corresponding focus was used throughout the experiment.

4.5 Design of Experiment

The four parameters included in the DOE were coater, casting speed, time delay, and exposure energy. The choice of the photoresist would dictate the range of exposure energy for the DOE. The choice of the photoresist would also dictate the type of developer used and therefore developer would not be part of the DOE.

The range of exposure energy was from dose to clear to +100% to achieve the target CD of 80 μm . Because of the dimension of the vias was in excess of 80 μm , measurements were done manually from the captured images or by software such as UTHSCSA 3.0. Fifteen sites per wafer were measured to generate within wafer statistics using the sampling plan in Figure 15.

Figure 15. Measurement sampling plan.

Besides exposure energy, there were other factors that needed to be included in the DOE. Once the screening tests were completed, the selected photoresist would be plumbed into the coater for automated dispense. However, because there were two different coaters with two different pumps, the coating behavior may be different and needed to be tested in the DOE. For this study, all the coating parameters were held constant except the machine type and casting speed. The assumption for the difference between the two coaters was their drying behavior. Casting speed was chosen as a process parameter because it influenced the drying behavior of the coated photoresist films. The range of casting speed was from 25 to 150 rpm.

The spin speed that controlled the photoresist thickness was not a variable because the target photoresist thickness was 50 μm . Instead, the spin speed was chosen based on spin curve data provided by the photoresist vendor that resulted in a 50 μm film.

One parameter that was not explored during screening but was essential during process characterization was the time delay between photoresist apply and expose. It was not a factor during screening because the time delay only affected CD. Photoresist manufacturer had recommended a one to two hours delay to stabilize the photoresist before exposure. However, it was not clear whether the time limit was an upper or lower limit. The idea of the delay was to re-hydrate and allow re-distribution of the solvents within the photoresist. In order to have a stable manufacturing process, time delay was included in the DOE with a range from 3.5 to 18 hours.

A full factorial DOE using JMP[®] would be used to explore the effect of each parameter to optimize the thick photoresist process with a target via dimension of 80 μm . The desired thick photoresist process should result in the straightest sidewall profile as well as the best control of via dimension. With two levels for coater, casting speed, time delay, and exposure energy, there were a total of 32 runs with one duplicate of each condition shown in Figure 16. The range of the levels for each parameter was selected based on the screening experiment results.

DOE - Full Factorial Design

Full Factorial Design

Responses

Add Response Remove N Responses...

Response Name	Goal	Lower Limit	Upper Limit	Importance
☒ CD MEAN	Maximize	.	.	.
☒ CD SIGMA	Minimize	.	.	.

Factors

Continuous Categorical Remove

Name	Role	Values
☒ COATER	Categorical	1 2
☒ CASTING SPEED	Continuous	25 150
☒ TIME DELAY	Continuous	3.5 18
☒ EXPOSE ENERGY	Continuous	2800 3400

Full Factorial Design
 2x2x2x2 Factorial
 Output Options

Run Order: Randomize

Number of Runs: 32

Number of Center Points: 0

Number of Replicates: 1

Make Table

Back

Figure 16. Full factorial DOE.

4.6 Verification

Final performance verification was done with scanning electron microscope (SEM) of the electroplated features. Straightness of the sidewall profiles was examined and was compared to features processed with the contact/proximity aligner.

CHAPTER FIVE RESULTS

5.1 Material Screening

The results of the screening tests are shown in Table 3.

Table 3. Screening Results.

Process		Parameter	Criteria	A	B	C	D
Environmental		Chemical Review	Comply with company EH&S regulations	Passed	Passed	Passed	Failed
Coat		Thickness	Single layer coating to 50 μm	Passed	Passed	Passed	N/A
		Cleanliness	"Cotton Candy" free	Passed	Passed	Passed	N/A
Expose		Dose to clear (positive)	<1500 mJ/cm ²	1500	Failed	N/A	N/A
		Dose to stay (negative)		N/A	N/A	500	N/A
Develop	TMAH	Time	<10 minutes	N/A	N/A	Passed	N/A
	KOH			Passed	N/A	N/A	N/A
Compatability		Photo	Use of reduction stepper	Passed	N/A	Passed	N/A
		Electroplating	No photoresist lifting and underplating during electroplating	Passed	N/A	Passed	N/A
		Removal	No residual photoresist	Passed	N/A	Failed	N/A

Photoresist D was eliminated at the start of screening upon receiving the MSDS because it contained glycol ether A and B which were known carcinogens and therefore not compatible for manufacturing. Photoresist B failed the screening test because it required too much dose to clear. The rule of thumb for setting the exposure energy for manufacturing was twice the dose to clear. Since the dose to clear was at 2100 mJ/cm^2 , a suitable manufacturing process would require exposure energy of higher than 4000 mJ/cm^2 . However, the maximum exposure energy for a reduction stepper in this study was set at 3500 mJ/cm^2 . Photoresist C failed the screening test because the stripping process in NMP after electroplating did not remove the photoresist cleanly as shown in Figures 17 and 18. The dark residual in Figure 17 indicated that organic material was still present at the sidewall because it was charged in the SEM. If the sidewall was clean, there should be no dark residual. The dark residual was confirmed to be organic because it was removable using a long oxygen reactive ion etch (RIE) shown in Figure 18.

Figure 17. SEM images of electroplated via structures using negative photoresist C.

Figure 18. SEM images of electroplated via structures using negative photoresist C after oxygen RIE.

Figure 19 shows another type of residual where large pieces of photoresist were clinging between two electroplated features. The gap between the features was about 80 μm . Most of the photoresist was removed with NMP leaving behind a shell. This type of residual was not removable even with an aggressive oxygen RIE.

Figure 19. SEM image of negative photoresist C residual between electroplated via structures after photoresist stripping.

Figure 20. SEM image of electroplated via structure using positive photoresist A.

Among the four thick photoresists, photoresist A was selected for further process characterization. Figure 20 shows a clean 35 μm electroplated copper feature after NMP stripping processed with photoresist A.

5.2 Focus Effect

In order to produce a very straight sidewall profile through 50 μm photoresist using a reduction stepper, it was desirable to set the focal plane as deep into the photoresist as possible. However, the reduction stepper only had a range of $\pm 50 \mu\text{m}$. A focus test was performed to determine if the reduction stepper could be operating at the maximum focus of $-50 \mu\text{m}$. Three focus matrix wafers were processed with focus offset ranging from 0 to $-50 \mu\text{m}$ shown in Figure 13. The results indicated that the maximum focus for the reduction stepper was indeed $-50 \mu\text{m}$. The stepper gave an error for tool malfunction when the focus was set beyond $-50 \mu\text{m}$. Furthermore, optical measurements of the dark band around the vias (Xo-Xi), as in Figure 14, for the focus matrix wafers

showed that the best focus condition was at $-50\text{ }\mu\text{m}$ because the width of the dark band was the smallest as shown in Figure 21. This dark band measurement represented the amount of curvature of the vias.

Figure 21. Focus matrix result.

5.3 DOE Results

The parameters for the DOE were coater, casting speed, time delay, and expose energy. The range of these parameters for the DOE is summarized in Table 4.

Table 4. Parameter Range for the DOE.

Parameters	1	2
	100	150
	3.5	18
	2800	3400

5.3.1 Coater 1 Results

Once all the measurement data was collected from the DOE, JMP® was able to construct a model that predicted the via dimension based on process parameters. The desirability function could even automatically set the process parameters based on the user's input on what parameters to be held constant.

Figure 22 shows the model prediction using Coater 1 while holding the via dimension at 80 μm . One interesting observation from the model was that the thick photoresist process was not a strong function of casting speed. The desirability function with respect to casting speed was a flat line. Casting speed was different from spin speed where spin speed controlled the final thickness of the coated film, casting speed controlled how fast the photoresist got spread across the wafer before spinning as well as the rate of evaporation of the photoresist. For a uniform spin coating, viscous photoresist needed to be cast almost to the edge of the wafer before spinning or the edge of the wafer would have thinner photoresist than the center. Photoresist was constantly evaporating during the casting period and therefore faster casting speed should result in less evaporation and slower casting speed should result in more evaporation and a drier film.

Figure 22. DOE prediction using Coater 1.

The reason casting speed was not a strong function was probably because Coater 1 had a very uniform drying behavior by design. The assumption that the casting speed had an influence in the thick photoresist was not valid.

The other observation was that the dependency on time delay was quite small up to about six hours. The time delay was attributed to re-hydration of the photoresist by the vendor. However, this effect was not well understood by the photoresist vendor. Future study would be necessary in order to determine the cause of the time delay.

With the use of the desirability function from the prediction profiler, the maximum desirability for CD was set to “match target” of 80 μm and the maximum desirability for standard deviation was set to “minimize” as indicated by the rightmost graphs in Figure 22. Once the coater parameter was locked for Coater 1, JMP[®] was able to find the appropriate values for the remaining three parameters within the boundary of the DOE to reach the maximum desirability.

The best process with Coater 1 would be to spin with a casting speed of 25 rpm, expose with the highest exposure energy of 3400 mJ/cm^2 and keep the time delay under six hours. The predicted CD from the model was 80.33 μm compared to a target of 80 μm with a standard deviation of 1.29 μm .

5.3.2 Coater 2 Results

Figure 23 shows the model prediction using Coater 2 while holding the via dimension at 80 μm . Unlike the prediction with coater 1, prediction with Coater 2 had a small sensitivity to casting speed where higher casting speed was desirable. However, because the sensitivity was small, it agreed with Coater 1 that the casting speed was not the cause of the difference between the two coaters. The performance difference between the two coaters was real. CD measurements from wafers processed with the same coating recipe with the two coaters vary by more than 5 μm . There were other differences between the coaters other than the drying behavior that needed to be investigated in order to determine the reason behind the CD variation. These parameters

included the exhaust flow, chemical feed line diameter, chemical pump size, and hot plate temperature control.

Figure 23. DOE prediction using coater 2.

The time delay sensitivity was opposite to that of Coater 1. The longer time delay resulted in smaller CD indicated that the Coater 2 photoresist continued to lose photosensitivity with time. The reverse sensitivity to time delay as compared to Coater 1 was another indication that the properties of the thick photoresists from the two coaters were different. Further investigation would be required to characterize the difference between the two coaters.

The best process with Coater 2 from the model prediction would be to spin with a casting speed of 150 rpm, expose with the highest exposure energy of 3400 mJ/cm² and keep the time delay above 10 hours. The predicted CD from the model was 79.62 μ m compared to a target of 80 μ m with a standard deviation of 0.97 μ m. A summary of the recommended process parameters from the two coaters are in Table 5.

Table 5. Summary of Recommended Process Conditions from the DOE.

Parameters	Coater 1	Coater 2
Casting Speed (rpm)	25	150
Time Delay (h)	<3	2-3
Exposure Energy (mJ/cm ²)	3400	3400
Exposure Time (s)	-50	-50
RUE (mJ/cm ² /h)	10	10

5.3.3 Coater Selection

Both sets of process conditions were capable to achieve the desired results of 80 μ m vias. However, weighing between process robustness and tighter tolerance, Coater 2 was selected as the process of record (POR) because the model predicted that the standard deviation of the via dimensions across the wafer would be lower. The desirability for Coater 2 (0.889) was also higher than that of Coater 1 (0.803). Although there was still sensitivity to time delay for the coater 2 process, the effect to CD could be modeled and controlled with adaptive process control (APC). The process

recommendation with APC would be to use Coater 2 with a casting speed of 150 rpm, a two to three hour time delay, and expose with 3400 mJ/cm^2 .

It was still necessary to have the process conditions defined for the non-POR coater as the backup tool in manufacturing. APC could be used to handle the difference in the time delay behavior between the two coaters to allow simultaneous processing utilizing both coaters.

5.4 Model Verification

The final process verification came with SEM pictures of the $35 \text{ }\mu\text{m}$ electroplated copper via structures using the Coater 2 process as shown in Figure 24. The sidewall profiles were quite straight even when the depth of focus of the reduction stepper was limited for the thick photoresist application.

The thick photoresist process defined by the DOE was then compared to the process using a contact aligner. The SEM images from the contact aligner in Figure 25 had straighter sidewalls than those from the reduction stepper in Figure 24. Features produced by the contact aligner did not show any roundness towards the top of the vias. The straightness of the sidewall from the contact aligner was due to wider depth of focus as well as broadband exposure wavelength as compared to the I-line reduction stepper. Since this thick photoresist was formulated for a contact aligner, it was no surprise that

the results from the contact aligner were better than the reduction stepper. However, the reduction stepper process still compared favorably.

Figure 24. SEM images of electroplated via structures using process conditions for Coater 2.

Figure 25. SEM images of electroplated via structures using contact aligner.

CHAPTER SIX CONCLUSIONS

A thick positive photoresist designed for contact aligners was shown to have satisfactory results in processing using a reduction stepper. SEM images of the electroplated copper structures confirmed that the reduction stepper could produce straight sidewall profile through 50 μm photoresist.

DOE results from the two different coaters used in this study yielded two different photolithographic processes. Although both processes were capable, Coater 2 process was selected as the process of record because of better within wafer variation. The difference between the two processes was attributed to the difference in the coating characteristics.

CHAPTER SEVEN

FUTURE WORK

In order to implement the recommended process conditions from the DOE, the CD sensitivity with respect to time delay needs to be characterized for the two different coaters. With this information, APC can be setup for the stepper to determine the time delay before expose and adjust the exposure energy accordingly to achieve the target CD.

Even with the implementation of APC, it will be necessary to continue investigating the cause of the time delay effect. CD APC for time delay is only valid if the correlation between CD and time delay does not change. It is therefore important to understand the reason behind the time delay effect and maintain or eliminate it.

Understanding the differences between the two coaters may also provide valuable information regarding the differences in the film properties. All these future efforts will further improve the process robustness of the thick photoresist process using a reduction stepper.

REFERENCES

1. A. Chiu, I. Croll, D.E. Heim, R.E. Jones, Jr., P. Kasiraj, K.B. Klaassen, C.D. Mee and R.G. Simmons, "*Thin-film inductive heads*," IBM Journal of Research and Development, **40** (3), pp. 283-300 (1996).
2. O. Shinoura, and T. Koyanagi, "*Magnetic thin film head with controlled domain structure by electroplating technology*," Electrochimica Acta, **42** (22-24), pp. 3361–3366 (1997).
3. B. Fay, "*Advanced optical lithography development, from UV to EUV*," Microelectronic Engineering, **61-62**, pp. 11-24 (2002).
4. J.J. Shamaly and V.F. Bunze, "*I-Line to DUV Transition for Critical Levels*," Microelectronic Engineering, **30**, pp. 87-93 (1996).
5. K. Leinonen, "*Patterning large-area devices with a 5:1 reduction stepper*," Nuclear Instruments and Methods in Physics Research A, **555**, pp. 59-64 (2005).
6. R. Dammel, Diazonaphthoquinone-based Resists, (SPIE Optical Engineering Press, 1993).
7. C.G. Wilson, "*Resists for Deep UV Lithography*," SPIE Professional Development, (2006).
8. G. Bleidiessel, G. Gruetzner, F. Reuther, S. Fehlberg, B. Loechel and A. Maciossek, "*Dependence of the quality of thick resist structures on resist baking*," Microelectronic Engineering, **41-42**, pp. 433-436 (1998).
9. P. Niedermann, H. Berthou, S. Zwickl, U. Schönholzer, K. Meier, C. Gantner and D. Kapp-Schwoerer, "*A novel thick photoresist for microsystem technology*," Microelectronic Engineering, **67-68**, pp. 259-265 (2003).
10. Y. Senu, A. Sekiguchi and Y. Miyake, "*Improved Resolution of Thick-Film Resist (Effect of Development Technique)*," Electronics and Communications in Japan, Part 2, **86** (7), pp. 50-60 (2003).
11. J.M. Shaw, J.D. Gelorme, N.C. LaBianca, W.E. Conley and S.J. Holmes, "*Negative photoresists for optical lithography*," IBM Journal of Research and Development, **41** (1/2), pp. 81-94 (1997).

12. W. He, C.R. Halberstadt and K.E. Gonsalves, "*Lithography application of a novel photoresist for patterning of cells*," *Biomaterials*, **25**, pp. 2055-2063 (2004).
13. A. Lebib, M. Natali, S.P. Li, E. Cambil, L. Manin, Y. Chen, H.M. Janssen and R.P. Sijbesma, "*Control of the critical dimension with a trilayer nanoimprint lithography procedure*," *Microelectronic Engineering*, **57-58**, pp. 411-416 (2001).
14. M. Chatzichristidi, I. Raptis, C.D. Diakoumakos, N. Glezos, P. Argitis and M. Sanopoulou, "*Strippable aqueous base developable negative photoresist for high aspect ratio micromachining*," *Microelectronic Engineering*, **61-62**, pp. 729-735 (2002).
15. C.A. Mack, D.A. Legband and S. Jug, "*Data Analysis for Photolithography*," *Microelectronic Engineering*, **46**, pp. 65-68 (1999).
16. A. Tay, W.K. Ho, J. Deng and B.K. Lok, "*Control of photoresist film thickness: Iterative feedback tuning approach*," *Computers and Chemical Engineering*, **30**, pp. 572-579 (2006).
17. Y.H. Joung, S.Y. Mun and S.J. Kang, "*Improvement of gate CD imbalance for a 0.35 μ m logic technology*," *Materials Science in Semiconductor Processing*, **7**, pp. 51-54 (2004).
18. S. Andre and A. Weill, "*Variable Numerical Aperture and Partial Coherence studies: Process Window and Proximity Effects*," *Microelectronic Engineering*, **30**, pp. 99-102 (1996).
19. G. Arthur and B. Martin, "*Sub-half micron contact hole definition by i-line optical lithography*," *Microelectronic Engineering*, **27**, pp. 279-282 (1995).
20. S. Postnikov, S. Hector, C. Garza, R. Peters and V. Ivin, "*Critical dimension control in optical lithography*," *Microelectronic Engineering*, **69**, pp. 452-458 (2003).
21. W.G. Oldham, S. Subramanian and A. R. Neureuther, "*Optical requirements for projection lithography*," *Solid-State Electronics*, **24** (10), pp. 975-980 (1981).
22. H.Y. Kang and A.H.I. Lee, "*Critical dimension control in photolithography based on the yield by a simulation program*," *Microelectronics Reliability*, in print (2005).
23. D. Fuard and P. Schiavone, "*Assessment of the critical dimension prediction accuracy for the lumped parameter model for resist lithography*," *Microelectronic Engineering*, **73-74**, pp. 53-58 (2004).

24. P.I. Hagouel, I. Karafyllidis and A.R. Neureuther, "*Dependence of developed negative resist profiles on exposure energy dose: experiment, modeling, and simulation,*" *Microelectronic Engineering*, **41-42**, pp. 351-354 (1998).
25. E. Cullmann, B. Loechel, A. Maciossek and M. Rothe, "*Advanced resist processing for thick photoresist applications,*" *Microelectronic Engineering*, **30**, pp. 551-554 (1996).