OPTIMIZATION OF IMAGE REVERSAL
.
OF POSITIVE PHOTORESIST

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INTRODUCTION

The technique of image reversal of diazide photoresist has been discussed in literature for more than ten years. This method of image reversal produces negative tone images in positive photoresist. Only recently has interest for negative photoresist. The image reversal process provides all the advantages of positive photoresist:

- ?? improved resolution
- ?? superior edge quality
- ?? safer, more reliable processing with aqueous-based chemicals in place of toxic, flammable organics
- ?? superior CD control and uniformity

Image reversal is being evaluated for application to the following:

- ?? rework techniques on multi-layer metal
- ?? metal lift-off techniques
- ?? multi-layer photoresist replacement
- ?? E-beam mask generation on photoresist

Previous works on image reversal have presented its feasibility as well as its potential for the microelectronics industry. However, no report to date has confirmed the image reversal process capability of producing consistent, high-quality results. This paper characterizes the image reversal process. Controlling operating parameters and limitations.

BACKGROUND

Briefly, the image reversal process can be described as follows. In the first step, a resisted photomask (diazoquinone/phenolic based, such as AZ1350J or Kodak 820) is imaged, converting the sensitizer to a substituted indene carboxylic acid.

After the initial exposure, the plate, the plate is baked for a specific time and temperature in an amine environment. The reaction that occurs during this bake cycle leaves the previously exposed area resistant to basic aqueous development and inert to subsequent exposures. A flood exposure of the entire plate causes the remaining sensitizer to convert to the indene carboxylic acid. These areas are then developed with the appropriate aqueous developer, thus producing a negative tone image.

Moritz and Paul[1] patented the negative-working positive photoresist process (the "Monazoline Process") in 1975. They claimed that the addition of monazoline (1-hydroxyethy-2-alkylimidazoline) to positive photoresist would result in a reversed image as described.

MacDonald et al[2] further modified this process by using a similar additive, imidizole. They proposed that the chemical reaction mechanism is a base catalyzed thermal decarboxylation during for the post-exposure-bake step. This mechanism was supported by their tests with mass spectroscopy, infrared experiments, NMR, thin layer chromatography and differential scanning calorimetry.

These findings provide an excellent understanding of what seemed to be a mystical process. However, problems were encountered with this technique. The additive catalyst once mixed with photoresist would not remain stable with the passage of time. Resists used for negative processing would have to be prepared shortly before exposing. Most photoresist users would be hesitant to consider using additives (potential contaminants) that could increase defect densities.

How can image reversal be accomplished without these inconveniences? MacDonald et al briefly mentioned in their publication that image reversal was possible in the presence of ammonia vapors during the post-exposure-bake cycle. This technique was confirmed by Long and Newman[3]. They experimented with the reversal process, utilizing solutions of tetramethyl ammonium hydroxide and tetramolamine. Although their experimental setup could have been more controlled, they did succeed in determining bake conditions necessary to minimize resist thickness loss (after bake, before development) to about 10% with the triethanolamine solution.

The most recent findings on this subject were presented at SPIE '85 by Alling and Stauffer.[4] They utilized Intec's "Star" process oven. This technique utilizes a vacuum oven capable of providing an "anime" atmosphere for the post-exposure bake step. Their results provided the first published information pertaining to production quality image reversal. They demonstrated with limited sampling:

- ?? CD variability within 0.28 um
- ?? CD submicron biasing of ±0.55 um
- ?? resolution of 1.0 um equal lines and spaces

No information has been presented on image reversal's effect on the following:

- ?? repeatability of critical dimension uniformity, movement and control
- ?? defect densities

Ultratech Photomask began investigating image reversal as a means of replacing negative photoresist. The negative process was unattractive because of the poor image quality produced and the hazardous chemicals needed for processing. Imidizole, added to Kodak 820, was examined and quickly rejected because of its instability with time and inconvenient preparation. The next alternative, an ammonia vapor atmosphere during the bake cycle, sounded promising. This procedure would utilize the same raw material blanks and developer used for positive image processing.

Preliminary experiments at Ultratech to demonstrate that ammonia vapors could catalyze the image reversal process utilized a petri dish filled with household ammonia in a convention oven. However unsophisticated this method was, the image reversal was accomplished. A prototype process was designed and built to test this method for production use. This process consisted of a vacuum oven capable of drawing in vapors from a concentrated solution of ammonium hydroxide and evacuating the vapors upon completion of the post-exposure bake. This prototype has proven to be safe, easy and reliable to use. The resulting quality of the reversed image was superior to the images produced in negative photoresist. The image reversal process has been used in production since May 1984 for negative 10X reticles.

Excellent image quality provided the incentive to investigate reversal quality on a 1X level. The Yield Engineering Systems "Yes 8" was used for this testing. Similar to the prototype oven described, "Yes 8" is equipped to use ammonia gas. It was believed that the gas would provide greater consistency and less opportunity for equipment corrosion. The process was optimized for CD control, uniformity, minimum resist loss, defect density and resolution.

EXPERIMENTAL PROCEDURES AND RESULTS

All the image reversal tests described below utilized the following:

Material

Type: 5" x 5" x 0.09" photomask blanks

Glass: Quartz, Low Expansion and Soda Lime

Photoresist: AZ 1350, -5000Å

Chrome: Anti-Reflective

Equipment

First Exposure: GCA Mann 3696 Photorepeater (435nm)
Tamarack Model 142 Contact Printer

Bake Cycle: Yield Engineering Systems Image
Reversal Oven with ammonia gas

Flood Exposure: Tamarack Model 142 contact printer

Process: APT Model 914
Develop - 45 seconds, Cyantek CC 200, 60%
Etch - (Cyantek CR3)
Strip - (Cyantek RS4)

Test Pattern

Array Size: 16.4 sq. in., 26 rows, 13 columns

Field: 50%, clear, 50% dark

Critical Dimension: 4 micron clear space and 4 micron clear dark line

CRITICAL DIMENSION UNIFORMITY

The first goal was to determine the bake cycle operating conditions to achieve the best critical dimension uniformity. Four plates were stepped with an exposure energy of 47.3 mJ/cm^2. A list of the CD test runs and operating conditions are shown in Table 1.

A Nikon 2I provided the measurement date for CD uniformity. Forty-eight points, evenly distributed to cover the full array, were measure. The statistical 3 sigma variance was calculated for each plate. The results were compared form plate to plate and are listed in Table 1.

Image reversal is confined with respect to bake temperature. Below 85°C the reversal will not occur. The resist also becomes unstable and degrades above 120°C. Therefore, the process must be maintained within these limits. Increasing the bake time or raising the temperature completes the reversal. Higher temperatures resulted in poorer critical dimensional uniformity as well as difficult resist removal in the plate corners.

The dark squares in the figure represent linewidths greater than the mean and the clear squares are less. It was believed that this trend was due to a non-uniform bake. The plates had all been baked in a metal holder on the floor of the oven. The heating coils are located by walls and under the floor of the chamber. The bake cycle takes place at a slight vacuum, thus there is little air movement to heat plates by convection. A temperature distribution through each plate results form conduction from the oven floor's heating coils. After inserting a rack in the oven, the problem was still apparent but less severe. This modification enabled critical dimension 3 sigma values of about 0.1 micrometers to be attained. Baking plates in a horizontal position resulted in CD 3 sigma values of less than 0.10 micrometers. This eliminated the trend of increasing linewidth through the plate.

The operating conditions determined to provide the best critical dimension uniformity are 95°C and 45-minute bake. All subsequent tests were conducted with these parameters.

EXPOSURE LATITUDE AND RESOLUTION

Two plates were stepped with an exposure matrix of 17.2 mJ/cm^2 to 103.2 mJ/cm^2 underwent image reversal with a subsequent flood exposure of 117 mJ/cm^2. Another plate was stepped with exposure energies ranging from 4.3 mJ/cm^2 to 43 mJ/cm^2 as a positive resist process control. The reticle used was a four-inch square die resolution target with L-bar patterns from 100 to 6 micrometers repeated over the entire die.

The two micrometer clear space in die centers of selected exposures was measured on an OSI linewidth measuring instrument before and after resist removal. The nominal hold exposure was identified. This was used as the stepping exposure for test to follow.

The image reversal process requires between two and three times the nominal exposure energy required for the standard positive process. However, this enables superior CD control, as can be seen by the relatively flatter curve for the image reversal process.

At the nominal exposure, the minimum geometry size capable of resolving throughout the entire die field was identified. Features of 0.8 micrometers (equal lines and spaces) were achieved at the nominal exposure. All greater line sizes fell linearly in place.

Scanning Electron Micrographs of the reversal product at nominal exposure were made. SEM's of positive and negative photoresist patterns at nominal exposure were made to compare resolution and edge quality. The swelling, characteristic of negative photoresist can be seen by the curving in the lines. The negative product resembles low hills. The images in the positive photoresist via the standard or image reversal process are steep and straight.

RESIST LOSS

Effect of Primary Exposure

Four plates were measured for resist thickness on a Rudolph FTM. These blanks were exposed through a simple mask (1/2 side clear, 1/2 side chrome) with 59, 117, 176 and 234 mJ/cm^2 on a Tamarack Contact Printer. After undergoing the image reversal process (flood exposure = 117 mJ/cm^2) and development, the remaining resist was remeasured. A control sample exposed at 53 mJ/cm^2 was prepared utilizing the standard positive process. Resist thickness was measured before and after processing. The results are summarized in Table 2. As can be seen, there is very little difference between the resist loss in the way processes.

Effect of Flood Exposure

Four plates were measured and exposed through the mask described above, using a 176 mJ/cm^2 dose. After the ammonia bake, the plates were flood exposed with 59, 117, 176 and 234 mJ/cm^2 respectively. The resist loss for each plate is listed in Table 3. Within this exposure range there is no effect of flood exposure variation on resist loss.

DEFECT DENSITY AND CRITICAL DIMENSION CONTROL

Six plates stepped at a nominal exposure of 73.1 mJ/cm^2 were prepared for defect inspection and CD control evaluation. Four plates were baked together at a time. Two plates from each bake lot were examined with a KLA 101 at 1.0 micrometer, single-scan fast speed for defect inspection. The Nikon 2I was used for CD measurement. These plates were compared with control tests from the standard positive process. The results are shown in Table 4.

The average defect density is greater for the reversal process. For 10X reticle production, 90% of these defects will not be detected because they are less than 5 micrometers in diameter. It is believed that the defect density can be brought to the level of the standard positive process. The reversal process was set up with the "yes 8" oven in another area away form the step and repeat camera. It is likely that the test plates became contaminated in the transfer.

CONCLUSIONS

1. The optimal conditions for the image reversal process are 45 minute bake at 95°C.

2. Image reversal consistently produces:
    - ?? CD uniformity 3 sigma values of about 0.08 micrometers
    - ?? CD means within 0.05 micrometers
    - ?? Defect densities
      -less than 1.9 defects/in.^{2}
      -less than 1.0 defects/in.^{2}
      for defects greater than 2 micrometers

    - ?? Resolution of 0.8 microinches equal lines and spaces at nominal exposure
    - ?? Approximately 10% resist loss after development.

3. There is no effect of varying flood exposure dose on resist thickness after development.

4. Image reversal requires between two and three times the exposure does of standard positive photoresist processing resulting in greater CD control.

REFERENCES

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Table 1: Critical dimension uniformity test conditions and results
($47.3\ mJ/cm^2$ exposure, $117\ mJ/cm^2$ flood exposure)

	Bake Time (Min.)	Temperature (°C)	Average CD Uniformity 3 Sigma Variance (Micrometers)
Baked Vertically on Oven Floor	90	75	Incomplete Reversal
	45	85	Incomplete Reversal
	60	85	0.283
	90	85	0.292
	120	85	0.217 (overbaked in corners)
	45	95	0.209
	60	95	0.228
	90	95	0.368
	120	95	0.441 (overbaked in corners)
	30	105	Incomplete Reversal
	60	105	0.663
	90	105	0.782
	120	105	2.01

Baked Vertically on Rack	45	95	0.140

Baked Horizontally on Rack	45	95	0.084

Table 2: Effect of initial exposure on remaining resist thickness

			Resist Thickness Remaining (%)		
			After Bake		
Initial Exposure (mJ/cm^2)	Flood Exposure (mJ/cm^2)	Initial Resist Thickness (nm)	Exposed Area	Unexposed Area	After Development
59	117	578	95.4	98.1	Incomplete Reversal
117	117	578	95.6	98.3	85.8
176	117	578	96.2	98.1	90.3
234	117	580	95.4	98.0	91.7
53*		579			95.7

*Positive Process Control

Table 3: Effect of flood exposure on remaining resist thickness

			Resist Thickness Remaining (%)		
			After Bake		
Initial Exposure (mJ/cm^2)	Flood Exposure (mJ/cm^2)	Initial Resist Thickness (nm)	Exposed Area	Unexposed Area	After Development
176	59	585	96.6	98.2	90.9
176	117	585	95.9	98.2	91.5
176	176	586	96.9	99.0	91.3
176	234	578	96.2	98.3	90.7
53*		578			95.8

*Positive Process Control

Table 4: Image reversal product quality and repeatability defects and critical dimensions

	Defect Data				CD Data	
	Clear Defects		Opaque Defects		Mean	3 Sigma
	1.0-2.0 um	>2.0 um	1.0-2.0 um	>2.0 um	(Micrometers)	(Micrometers)
Positive Controls	3	2	8	9	5.110	0.083
	2	1	13	15	5.120	0.097
	4	1	10	11	5.065	0.076
	2	2	13	6	5.076	0.072
	0	0	9	5	5.00	0.037
	2	0	8	6	4.95	0.044