KMPR Photoresist Process Optimization Using Factorial Experimental Design

Harris R. Miller and Donald W. Johnson

MicroChem Corporation, 1254 Chestnut St., Newton, MA 02464 USA

Satoshi Mori

Nippon Kayaku Co., Ltd., 2-8 Shimo 3-Chome, Kita-Ku, Tokyo 115-0042

MicroChem Corp. and Nippon Kayaku Co., Ltd. have jointly developed a new, photoimageable coating composition for use in fabricating a wide variety of micro-electromechanical systems (MEMS) and optical MEMS. This chemically amplified thick-film photoresist, known as KMPR, has many of the same high-aspect ratio photo imaging properties as solvent developable SU-8, but can be developed in a conventional aqueous alkaline developer (TMAH) and readily stripped from the wafer.

Single-factor experimental methods rarely find the optimum performance of a photoimageable coating efficiently and often fail to detect the interactions so common in complicated photochemical systems. By combining the settings of several factors *simultaneously* in an array (experimental design), it is possible to separate out the main effects and their interactions.¹

This paper presents the optimization of KMPR for contact alignment and near diffraction-limited, thick film reduction stepper applications. A Sequence of Taguchi style, half-factorial experimental designs was used to evaluate the process parameters for a 5 and 50 μm thick film exposed on a contact aligner followed by a third half-factorial design for a 10 μm thick film of KMPR photoresist exposed on a 365 nm, 0.40 N.A. stepper. Independent factors, such as: soft bake time, focus, exposure dose, initiator activation time (post-exposure bake time), developer time and delay time were evaluated.

1. Introduction

Photoresist materials are designed to be radiation-sensitive, which may also impart a thermal sensitivity. Therefore, it is important that any heat treatments, that the photosensitive composition receives, do not produce an insipient thermal activation or decomposition reaction². Immediately after coating, the photoresist is normally “soft baked” to set the film by removing or reducing the solvent content. The maximum bake temperature for this process step can be determined by thermogravimetric analysis (TGA) or by differential thermal analysis (DTA), however empirical analysis is more common since retained solvent in the photoresist coating can lower the photoresist T_g and increase developer dissolution. Therefore, retained solvent in the photoresist coating can have a great impact on the lithographic performance.

After the photoresist has been exposed to actinic radiation, a latent image is produced by a chemical reaction, which continues to react slowly at room

temperature. Chemically amplified photoresists, such as KMPR, require a post-exposure bake step (PEB) to accelerate this acid catalyzed polymerization reaction, to drive this reaction to completion and to control the environment of the exposed film. The effects of the PEB can be further complicated by the diffusion of the photo-acid in the resist outside the region of the exposure. However with KMPR the diffusion of the cationic photo-acid generator (PAG) has been found to be negligible for linewidths greater than 70 nm³.

Yet another method for controlling the post-exposure process condition is the use of a time delay between the exposure and the post-exposure bake steps. This type of post-exposure condition is believed to control the lateral diffusion of the PAG and therefore impact resolution. For this reason, studying the delay (“relaxation”) time was an important consideration.

The development time for negative-acting photoresists can be determined analytically or empirically and both methods express either a

dissolution rate or a "clearing time", which is an indication that the relatively large areas of unreacted photoresist, visible to the naked eye have been removed from the wafer. Because resist dissolution properties are highly dependent on the various development methods and printing geometries, we have chosen to include the effects of development time in our study.

Because of the complexity of the photoresist composition and its application, analytical results and empirical studies do not always agree. This is because of the highly *interactive* nature of the many processing parameters. For this reason, a systematic, orthogonal or "fair" approach was taken to investigate not only the main effects of each parameter, but also to study the equally important interaction of two parameters. In order to study both the main effects *and* the interactions, a fully "crossed" experiment is used, where all combinations of two or more parameters is tested. This "fully saturated" experiment can detect the significance of individual parameters, as well as two-way, three-way and four-way interactions. The relationship for the number of trials (T), parameters (F) and levels (L) in an experiment of this type is shown in Equation 1.

$$T = L^F \quad (1)$$

For example, the number of trials for a fully saturated experimental design with two levels (low and high) and four parameters (factors or independent variables) would be 2^4 (16) trials. Likewise a fully saturated experimental design with 8 independent variables would be 2^8 (256) trials. It is easy to see how quickly the number of trials for this type of experimental design would quickly spiral out of control. However, it is common in the early stages of an investigation, where there are so many factors to be considered that to run a full factorial experiment, even with all factors at two levels, would require too many trials⁴.

Another option is to execute a partial factorial design; where only a fraction of the total number of possible trials is tested. This technique still reveals both main effects and two-level interactions, but gives up higher order, three-way and four-way interactions. This trade-off is acceptable since it is common that when any interaction becomes important (significant) at least one of the main effects will also be significant. Also, higher order

interactions are often difficult to interpret and therefore, less important in the final analysis.

Fractional factorials are efficient experimental designs and are commonly used instead of a full-factorial design. The relationship between the number of trials for a fractional factorial can be shown below in Equation 2,

$$T = L^{F \cdot n} \quad (2)$$

where n represents the portion or fraction of the full-factorial. For example, a half-factorial 4-factor design would be $2^{4 \cdot 1}$ (8) trials and a quarter-factorial 8-factor design would be $2^{8 \cdot 4}$ (16) trials. Reducing the number of trials from 256 to only 16 still allows for the detection of two-way interactions, but confounds (confuses) some of interactions with one another, however, it is often easy to resolve this conflict with as little as three or four confirming experiments. Therefore, it is easy to see how powerful these designs are and how little tradeoff exists.

2. Procedure

The list of factors, which can be evaluated in an experimental design, are endless and the experimental designs are numerous. For simplicity, the number of levels was limited to only two (low and high or none and some) and the number of factors chosen was four. Therefore, a half-factorial design requires eight trials for completion. Replicates were not necessary since the error is calculated directly, provided that no more than two interactions were to be studied.

Table 1. Half-factorial experimental design for a 50 μ m KMPR Coating (times are in minutes, temperature in $^{\circ}$ C)

Trial	Soft Bake Temp	Soft Bake Time	PEB Temp	PEB Time	Minimum Resolution	Dose to Print	Minimum CD no Bias
1	80	10	80	1	25	600	45
2	100	10	80	1	25	600	45
3	80	20	80	10	14	600	40
4	100	20	80	1	20	430	40
5	80	10	100	10	20	430	55
6	100	10	100	1	13	600	20
7	80	20	100	1	15	600	25
8	100	20	100	10	13	600	20

The factors chosen for the first investigation, shown above in Table 1 are: soft bake time, soft bake temperature, post-exposure bake (PEB) time and PEB temperature. The factors for the two follow up investigations were soft bake time, post-

exposure bake time, delay “relaxation” time and developer time. The levels for each factor were deliberately set to a broad range and differed by as much as 100% between the low and high settings.

For small experimental designs, it is important to avoid “dead cells” or trials that produce no measurable result at all. For this reason, the maximum soft bake and post-exposure bake temperatures were determined empirically prior to performing this experimental design by measuring the amount of time required for the unexposed KMPR photoresist to be removed from the wafer surface in a developer solution of 0.26 N tetramethylammoniumhydroxide (TMAH). Figure 1 shows the response of clearing time for a 50 μm coating of KMPR photoresist, which had been baked for 15 minutes at each temperature. Based on these results, 105°C was found to have an impact on the KMPR clearing time. Therefore, all of the wafer bake treatments for this test were conducted at 100°C.

Figure 1. Developer clearing time for a 50 μm KMPR coating in 0.26 N TMAH Developer

Delay (“relaxation”) steps are built-in, user-defined process delays, placed at various steps in the process. Often, these delay times can be found between the soft bake and the exposure step, between the exposure step and the PEB and between the PEB and the develop step. For this investigation, the fourth factor was the incorporation of a 15-hour time delay between the exposure and the PEB steps.

Exposure dose is yet another factor which is often high on the list of factors to be tested. However, depending on the user, exposure can either be a response (dependent variable) or a factor (independent variable). Also, because it is easy to

produce a large set of exposures on a given wafer, exposure dose was not included in this design as a separate factor (independent variable).

Photoresist film thickness can also have a significant affect on the outcome of many experimental designs. Therefore, it would be logical to incorporate film thickness as a factor in a design. However, large changes in film thickness require significant differences in exposure and bake conditions, which if incorporated into a single experiment would lead to un-measurable wafers or dead cells. For this reason, three separate, sequential experimental designs were conducted at film thicknesses of 5, 10 and 50 μm . The trials were conducted in the order shown in Tables 1, 3 & 6 and analyzed using a statistical analysis package known as JMP (SAS Institute Inc., Cary, NC).

Table 2. Effects Table for Minimum CD in a 50 μm KMPR Coating

Effect Tests

Source	Nparm	DF	Sum of Squares	F Ratio	Prob > F
SB Time(10,20)	1	1	55.125000	4.6226	0.0842
PEB Temp(80,100)	1	1	66.125000	5.5451	0.0652

Table 3. Half-factorial experimental design for a 5 μm KMPR Coating (times are in minutes except relaxation time, which is in hours)

Trial	PEB Time	Soft Bake Time	Relaxation Time	Develop Time	Minimum CD	Minimum Dose
1	1	10	0	6	4.0	225
2	2	10	0	8	3.0	200
3	1	20	0	8	4.0	200
4	2	20	0	6	3.0	200
5	1	10	15	8	4.0	250
6	2	10	15	6	3.0	150
7	1	20	15	6	4.0	175
8	2	20	15	8	4.0	225

Table 4. Effects Test for Minimum CD in a 5 μm KMPR Coating

Effect Tests

Source	Nparm	DF	Sum of Squares	F Ratio	Prob > F
PEB Time	1	1	1.1250000	9.0000	0.0577
SB Time	1	1	0.1250000	1.0000	0.3910
Relaxation Time	1	1	0.1250000	1.0000	0.3910
Develop Time	1	1	0.1250000	1.0000	0.3910

Table 5. Effects Test for Minimum Dose in a 5 μm KMPR Coating

Effect Tests

Source	Nparm	DF	Sum of Squares	F Ratio	Prob > F
PEB Time	1	1	28.12500	9.0000	0.0955
SB Time	1	1	3.12500	1.0000	0.4226
Relaxation Time	1	1	3.12500	1.0000	0.4226
Develop Time	1	1	78.12500	25.0000	0.0377
PEB Time*SB Time	1	1	153.12500	49.0000	0.0198

Table 6. Half-factorial experimental design for a 10 μ m KMPR Coating (times are in minutes except relaxation time, which is in hours)

Trial	PEB Time	Soft Bake Time	Relaxation Time	Develop Time	Bottom CD
1	1	10	0	6	2.68
2	2	10	0	8	3.02
3	1	20	0	8	2.80
4	2	20	0	6	2.68
5	1	10	15	8	2.67
6	2	10	15	6	2.61
7	1	20	15	6	2.77
8	2	20	15	8	2.68

The results are plotted in Figures 2, 3 & 4, which show the main effects for each factor (*ex.* post-exposure bake time, soft bake time, relaxation time, developer time, etc.) and for multiple responses (*ex.* minimum CD, bottom CD, etc.). In order for a factor to be significant (meaningful) the "Prob>F" must be smaller than 0.05 (for a 95% confidence) or 0.10 (for a 90% confidence). The error bars on the effects plots indicate the 95% confidence intervals, the vertical dotted lines indicate the user defined settings of each independent factor and the response values indicate the predicted value with the $\pm$ 95% confidence interval.

Figure 2. Effects Plots for a 50 μ m KMPR Coating

Figure 3. Effects Plots for a 5 μ m KMPR Coating

Figure 4. Effects Plot a 10 μ m KMPR Coating

2.1 50 μ m Resist Process

The wafers were prepared as shown below.

- Eight, 100 mm silicon wafers were spin-coated with KMPR 1050 photoresist for 60 seconds at 1600 rpm.
- Four of the wafers (Trials 1, 3, 5 and 7) were soft baked @ 80°C and the remaining four wafers (Trials 2, 4, 6 and 8) were soft baked @ 100°C.
- Edge bead was removed using a syringe of EBR PG and spinning the wafer for 10 seconds at 600 rpm, followed by an additional 30 seconds at 1000 rpm.
- The wafers were baked again for 60 seconds at 65°C to prevent mask sticking and exposed using an AB-M 10 mW/cm² mercury vapor source, filtered with a 360 nm long-pass cutoff filter and a variable transmission resolution mask for 360-1200 mJ/cm² under 15 psi of vacuum contact.
- The wafers were post-exposure baked according to Table 1, developed for 6 minutes in 0.26 N TMAH, rinsed in de-ionized water and air-dried.
- The wafers were scribed, placed in the freezer (~-14°C) for 5 minutes and then cleaved for cross sectioning.
- The cleaved wafer sections were positioned at right angle to the microscope objective and measured for Minimum CD, Minimum CD no bias and line width (CD) using a dark-field, 1:1 line/space array.

2.2 5 μ m Resist Process

The wafers were prepared as shown below.

Two factors: soft bake and post-exposure bake temperature were replaced with two new factors: post exposure delay ("relaxation") time and developer time. The KMPR film thickness was also reduced to 5 μm by a change in viscosity and spin speed as shown below.

1. Eight, 100 mm silicon wafers were spin-coated with KMPR 1005 photoresist for 60 seconds at 4000 rpm.
2. Four of the wafers (Trials 1, 2, 5 and 6) were soft baked for 10 minutes @ 100°C and the remaining four wafers (Trials 3, 4, 7 and 8) were soft baked for 20 minutes @ 100°C
3. Edge bead was removed using a syringe of EBR PG and spinning the wafer for 10 seconds at 600 rpm, followed by an additional 30 seconds at 1000 rpm.
4. The wafers were baked again for 60 seconds at 65°C to prevent mask sticking.
5. The wafers were exposed using an AB-M 10 mW/cm² mercury vapor source, filtered with a 360 nm long-pass cutoff filter and a variable transmission resolution mask for 255-850 mJ/cm² under 15 psi of vacuum contact.
6. The wafers were left to "relax" for 15 hours at room temperature (Trials 5-8) or post exposure baked directly (Trials 1-4) according to the post-exposure bake times in Table 3.
7. The wafers were puddle developed in 0.26 N TMAH according to the developer times in Table 3, rinsed in de-ionized water and air-dried.
8. The wafers were scribed, placed in the freezer (~14°C) for 5 minutes and then cleaved for cross sectioning.
9. The cleaved wafer sections were positioned at right angle to the optical microscope objective and measured for Minimum CD using a dark-field, 1:1 line/space array.

2.3 10 μm Resist Process

The wafers were prepared as shown below.

No changes in factors, levels or layout were made for this duplicate experimental design other than KMPR film thickness, which was changed to 10 μm . However an important change in the exposure tool was made from the previously used broadband contact lithography to a 365nm 5X reduction stepper.

1. Eight, 100 mm silicon wafers were spin-coated with KMPR 1010 photoresist for 30 seconds at 3000 rpm.
2. Four of the wafers (Trials 1, 2, 5 and 6) were soft baked for 10 minutes @ 100°C and the remaining four wafers (Trials 3, 4, 7 and 8) were soft baked for 20 minutes @ 100°C
3. A focus-exposure matrix using an exposure range of 720 to 1220 mJ/cm² and a focus range of +2 to -10 μm was produced on an ASML 5200/45 (365nm) 5X reduction stepper (N.A. 0.40).
4. The wafers were left to "relax" for 15 hours at room temperature (Trials 5-8) or post exposure baked directly (Trials 1-4) according to the post-exposure bake times in Table 6.
5. The wafers were puddle developed in 0.26 N TMAH according to the developer times also in Table 6, rinsed in de-ionized water and air-dried.
6. The wafers were sputtered with 100 Å of gold and measured using a Leo 982 Scanning Electron Microscope (2kV, 60° viewing angle, 7 mm working distance).
7. Bottom critical dimension (CD) was measured for 1.25, 1.50, 1.75 and 2.0 μm isolated line features.

3. Results and Discussion

3.1 50 μm Resist Process

Both the soft bake time and the post exposure bake temperature were found to be significant (meaningful) for the ranges chosen using a 50 μm coating of KMPR, while the soft bake temperature and the post exposure bake time were not significant at all. This was found to be true for obtaining the minimum CD, but none of the factors tested were found to be significant for either dose to print or the minimum *unbiased* CD. Based on this data and some mask sticking that was observed at the lower, 80°C temperature, it was decided that subsequent experiments would be conducted using a soft bake time of 20 minutes and a soft bake temperature of 100°C. For processing convenience, the post-exposure bake temperature was also set at 100°C. Follow up experiments (not shown here) enabled us to further narrow the optimum post-exposure bake time to 2 minutes at 100°C.

3.2 5 μm Film Thickness

Post-exposure bake time was the only significant (meaningful) factor for influencing minimum CD, which allowed for a smaller CD size to be printed with the longer, 2-minute post-exposure bake time. A strong interaction was also detected between the soft bake and the post-exposure bake times but impacted only exposure dose and not minimum CD. This means that simply increasing the post-exposure bake time may not produce the optimum result. For example a long, 20-minute soft bake time combined with a short 1-minute post-exposure bake time is almost as effective as the opposite combination (10 minute soft bake time and 2 minute post-exposure bake time). When measuring the minimum CD printed on a 5 μm coating, the impact of soft bake time, developer time and relaxation time were all found to be insignificant, which means that these parameters would affect exposure latitude, but not the final result (minimum CD).

Table 7. Effects Test for Bottom CD in a 10 μm KMPR Coating

Effect Tests

Source	Nparm	DF	Sum of Squares	F Ratio	Prob > F
PEB Time	1	1	0.00081474	0.0464	0.8495
SB Time	1	1	0.00034084	0.0194	0.9020
Relaxation Time	1	1	0.02461544	1.4004	0.3583
Develop Time	1	1	0.02155355	1.2262	0.3835
Relaxation Time*Develop Time	1	1	0.02907293	1.6540	0.3272

3.3 10 μm Film Thickness

It is clear from the effects table (Table 7) that none of the factors or their interactions was significant for this test. Figure 4 illustrates the same conclusion graphically from the shallow slopes of each effect plot and the very large error bars associated with each plot. This was quite surprising considering that an order of magnitude change was made for both bake times. The exposure-PEB delay ("relaxation") time was also found to have no impact on bottom CD. The same low-level response was also seen for developer time, which had no impact on CD at all even though the slope of this plot appears greater.

Although no change in bottom CD was found from some very wide swings in process conditions, a greater dependence on focus and exposure latitude was expected. Exposure latitude was not measured for each process condition in the experimental design because focus was already established as a significant factor for controlling bottom CD especially for the very high aspect ratio structures

generated by the 10 μm thick coatings (See Figure 5). A Bossung curve (Figure 6) was generated from the focus exposure matrix for trial 1 (10 minute soft bake, 1 minute post-exposure bake, no relaxation time and a 6 minute developer time) and exposure was found to have a minimal affect on bottom CD. It is also apparent from this plot that the slope of the curve for CD vs. exposure is low, indicating a small or insignificant impact in the range of 820 to 1170 mJ/cm^2 . The focus and exposure latitude for Trial 1 (the shortest process conditions) was plotted with each contour representing a CD value.

Figure 5. Experimental Design Matrix of 2 μm isolated lines in a 10 μm KMPR coating exposed on an ASML 5200/45 stepper (N.A. 0.40)

Figure 7 shows the focus and exposure process window for a 2 μm bottom CD $\pm 10\%$ (1.8-2.2 μm). Again, it is surprising to see such a small dependence of CD on exposure, especially for such high-aspect ratio structures. However these types of structures do show a significant dependence on

Figure 6. Bossung Curve for a 10 μm KMPR Coating Figure 7. Focus-Exposure Matrix for $\pm 10\%$ CD Control for a 2 μm feature in a 10 μm KMPR Coating Figure 8. Focus and Exposure vs. CD for 2 μm feature of KMPR in 10 μm Coating. (1000, 1040, 1140 mJ/cm^2 and -6 , -4 & -2 μm)

focus setting. Typically a focus setting, which places the point of focus 40% into the depth of the photoresist coating, is common. For a 10 μm coating of KMPR, this would place the optimum focus setting at -4 μm . The visual impact of focus setting and exposure dose on sidewall profile of the 2 μm feature can be seen in Figure 8. Here it can be seen as the stepper focuses into the depth of the KMPR coating, the CD decreases at the point of focus.

It is surprising to see such a robust process and a small impact on CD from such large (100%) changes in process conditions. A $\pm 10\%$ CD control was achieved with a ± 250 mJ/cm^2 change in exposure dose and a ± 2 μm change in focus setting for 2 μm features in a 10 μm coating of KMPR. Normally, this amount of process latitude would be very desirable for patterned features with aspect ratios of only 1:1 (height:width); since as the aspect ratio increases the sensitivity to process conditions also increases. However, this was not the case with KMPR and 5:1 aspect ratio structures were produced with a very broad process and exposure latitude. The smallest isolated structure that was produced in the focus and exposure matrix was 1.25 μm (aspect ratio 8:1). All of these structures were produced from a single exposure and focus setting and without focus drilling.

The critical dimension (CD) of a 2 μm isolated feature in a 10 μm KMPR coating was the principal response for these stepper exposures. More dense structures, such as 1:1 pitch, were resolved but with some distortion. This distortion was caused by what is called "stiction", which indicates the lateral impact of developer surface tension on small printed structures. Since KMPR uses an aqueous developer, the drying forces tend to distort these well-formed resist structures. For this reason, the incorporation of a surfactant in the developer, the gradual replacement of water with alcohol or the complete replacement of the aqueous developer with a solvent developer is recommended.

The effect of process conditions on mask linearity and bias can be seen in Figure 9, which shows two trials: trial 1 (all low settings) and trial 8 (all high settings) together. No apparent difference can be seen between the two graphs, which represent the extremes in processing conditions. The relationship is linear in the range of 1.25 to 2 μm features and has a positive bias of 0.2 μm .

Figure 9. Focus and Exposure vs. CD for 2 μm feature of KMPR in 10 μm Coating

4. Conclusion

Because no significant differences were seen with the delay "relaxation" time (exposure to post-exposure bake), we might conclude one of two things: that the acid catalyzed cross-linking reaction does not proceed at room temperature or that the reaction is already completed after 15 hours and the post-exposure bake, which took place after the room temperature storage had no effect. In order to resolve this issue, a differential scanning calorimeter (DSC) trace is recommended, which would allow us to separate out the irreversible reaction conversions at varying temperatures. This analysis is key to resolving the optimum post-exposure bake temperature over a wider range of temperatures, including room temperature. In the absence of further analysis, it is clear that since none of the parameters were significant, the shortest, lowest, or fastest combinations would be the most desired. This means that for a 10 μm coating of KMPR, the optimum process conditions are summarized in Table 8 below.

Table 8. Optimum Process Conditions for 10 μm KMPR

Soft Bake Temperature ($^{\circ}\text{C}$)	100
Soft Bake Time (min.)	10
Exposure Dose (365 nm mJ/cm^2)	820
Focus Setting (μm)	-4
Post exposure bake temp	100
Post exposure bake time	1
Developer time (min in 0.26 N TMAH)	6

A statistical experimental analysis was applied to three different film coatings of KMPR. In each case, the answer was the same, "a robust process". It is also clear that separating out multiple designs for each film thickness was useful, even though most of the factors were shown to be insignificant. Normally, when a statistical test is conducted and the conclusion is "no difference detected" the beta-risk (not the alpha-risk) controls the probability of making the wrong conclusion. Therefore by running sequential designs, a greater sample size is generated and the investigator is better protected against accepting the "null hypothesis". In simpler terms, there is a risk in stating that there is no difference, when one actually exists. The risk is that you just failed to find it.

5. Acknowledgements

The author would like to thank Keith Best and Binder Mann from ASML Special Applications for their exposure & processing support and Jeff Walling at MicroChem Corp for the great SEMs.

6. References

1. "Applying Statistics to Solving Chemical Problems", Chemtech, 17, 167-169 (1987).
2. L. Thompson, C. Willson & M. Bowden, "Introduction to Microlithography Second Edition", Am. Chem. Soc. Washington, D.C., 317-320 (1994).
3. W. Hinsberg, F. Houle, M. Sanchez & G. Wallraff, "Chemical & Physical Aspects of the Post-Exposure Baking Process used for Positive-tone Chemically Amplified Resists", IBM J. Res. & Dev. Vol. 45 No. 5, September (2001).
4. A. Rickmers & H. Todd, "Statistics an Introduction", McGraw-Hill Book Company, New York, NY, 342 (1967).