0305-320 Characterization of Positive Photoresist

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ABSTRACT

The objective of this experiment is to determine the responses of lithographic sensitivity, contrast and thickness loss of positive photoresist as a function of the input process parameters. To efficiently determine the responses, a designed experiment is needed. The input process parameters are defined as pre-bake temperature, post-bake temperature and development time. A central composite design is used for the experiment which allows the analysis of the main effects response, the main effects quadratic, cubic and quartic response, and the interaction of main effects. It was found that thickness loss is a function of the pre-bake temperature, and development time. The dose to clear is a function of pre-bake temperature, post-bake temperature, development time, and the interaction of pre-bake and post-bake temperature. Lastly, the contrast is a function of pre-bake temperature, post-bake temperature, the interaction of pre-bake temperature and post-bake temperature, and the post-bake temperature squared. With the model equations of the outputs the inputs were set to maximize the contrast, minimize the thickness loss and minimize the dose to clear. To achieve the desired outputs, the pre-bake and post-bake temperature is set to 100 degrees Celsius and the development time is set to 50 seconds.

Keywords: Design of experiments, Positive Photoresist, Central Composite Design

1. INTRODUCTION

To carry out a photolithography process efficiently with good throughput it is necessary to know the characteristics of the photoresist in order to maximize the contrast of the photoresist, minimize the thickness loss of the photoresist from before and after development and to minimize the dose to clear. The contrast should be maximized in order to ensure a large difference between exposed and unexposed areas. The thickness loss should be minimized in order to ensure that the photoresist is thick enough for future processing. The dose to clear should be minimized in order to reduce the cost of exposure. In order to efficiently characterize the photoresist a designed experiment is required. A designed experiment allows one to know exactly what to do once the experiment is being carried out, rather than just randomly running experiments and hoping to notice a trend. A designed experiment also allows one to easily analyze the results using statistical methods.

2. THEORY

2.1 Chemical Properties of Positive Photoresist

Photoresist is composed of three main components, a resin, a photoactive compound, and a solvent. With photolithography processes with exposure to a mercury arc-lamp at i-line (365 nm) or g-line (436 nm) a positive photoresist with a novolac resin is typically used. The resin gives the photoresist the majority of its physical thin-film properties. The photoactive compound gives the photoresist the characteristic of being sensitive to light. In positive photoresist used at g-line and i-line the photoactive compound is diazonaphthoquinone (DNQ). DNQ is not soluble to an aqueous developer. However, when the DNQ is exposed to ultraviolet light undergoes a chemical reaction that causes it to become base soluble chemical. The chemical reaction of DNQ is illustrated in figure 1.

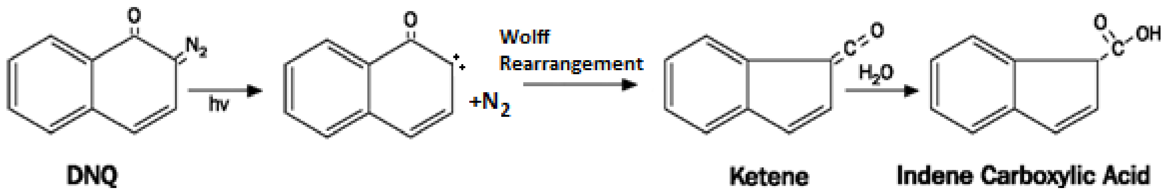

Figure 1. Chemical reaction of DNQ when exposed to light.

The chemical reaction that occurs when DNQ is exposed allows for the critical chemical property of positive photoresist, soluble where it has been exposed and insoluble where it hasn’t been exposed. The last part of the photoresist is the solvent. The solvent causes novolac resin to flow. If the solvent is not present the novolac resin will not flow.

The pre-bake during the exposure process is to evaporate most of the solvent, reducing the solvent concentration to about 5%. The developer’s rate of attack on the photoresist is primarily dependent on the amount of solvent in the photoresist. Thus, if the photoresist is pre-baked at too low of a temperature, the developer will develop the photoresist too fast. If the pre-bake temperature is too high, the photoactive compound will undergo reaction rendering the photoresist less photosensitive during exposure. The post-exposure bake is applied to the wafer because standing-waves in the resist-film cause an uneven distribution of PAC in the photoresist after exposure. The post-exposure bake causes the PAC to diffuse from unexposed regions to resist. This results in an averaging of PAC across the exposed and unexposed boundary.

2.2 Photoresist Characteristics

Photoresist has several measureable characteristics that can be altered by the photolithography process and settings for the different steps in the process. Three of these characteristics are contrast, thickness loss and dose to clear (sensitivity). In order to measure all three of these characteristics a plot is created of normalized thickness on the y-axis and the natural lose of the dose on the x-axis. The normalized thickness is the thickness, denoted by t, divided by the average initial thickness, denoted by t_0. Figure 2 shows an example plot.

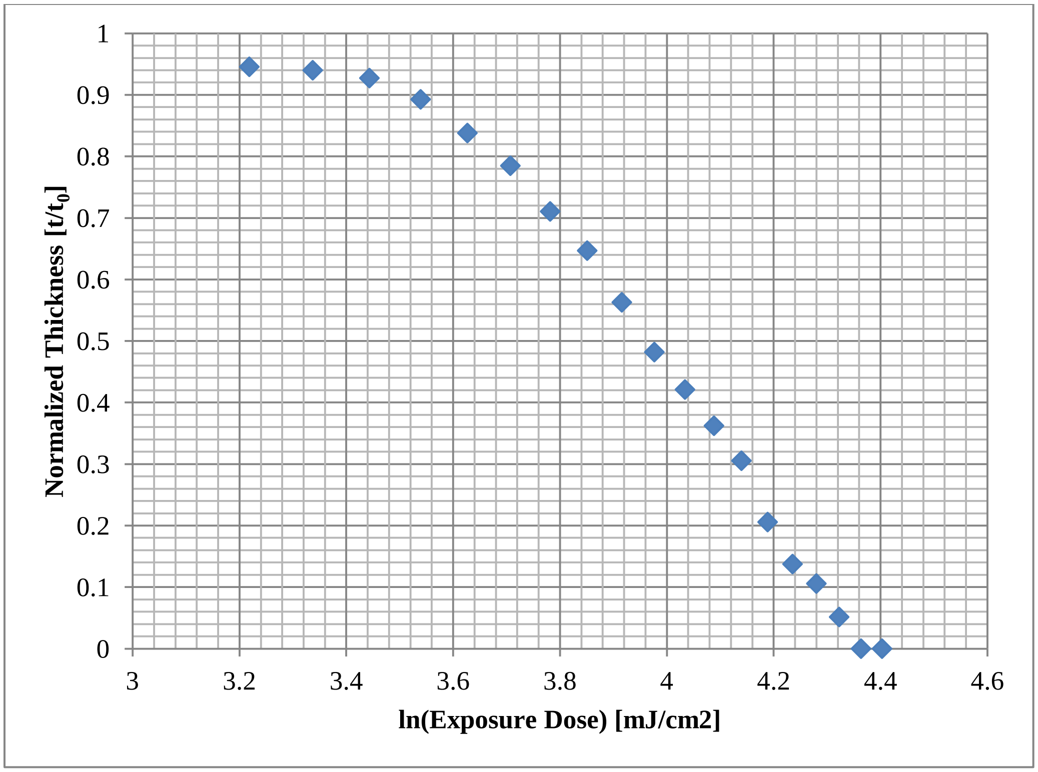

Figure 2. Example plot of normalized thickness vs. the natural log of the exposure dose.

In order to find the thickness loss it is simply the initial average thickness of the photoresist minus the post-development average thickness of the photoresist. Equation 1 describes how to find the thickness loss.

$$thickness\ loss = t_0 - t_{avg} \tag{1}$$

The thickness loss could also be found from the graph by taking the distance of the gap between a normalized thickness of one and the horizontal portion of the graph and multiplying the result by the average initial thickness.

The contrast of the photoresist is described by the slope of the negative sloping linear portion of the graph in figure 2. As such, the contrast is the slope of that linear portion. The best way to get the slope is to perform a least squares regression on the linear portion of the graph. Equation 2 describes the formula for the contrast (γ) of the resist.

$$\gamma = \frac{\Delta[t/t_0]}{\Delta[\ln(\text{dose})]} \tag{2}$$

The dose to clear is the minimum exposure required to fully expose the photoresist. Dose to clear can be seen on the graph in figure 2 as the point where the normalized thickness is zero. Using the linear equation for the linear part of the graph, one can solve for the x-intercept of the line. This would give the natural log of the dose to clear.

2.3 Design of Experiment

A central composite design (CCD) was used for this experiment. The central composite design allows for the required information, main effects and required interaction with a zero point and two extreme points for each factor. This design is also five levels. This would allow analysis of up to quartic effects; however this is very unlikely to occur. By using the central composite design to get the required information it is possible to run the experiment in 15 runs with 3 additional zero points for residual error estimation. If the experiment was a 3^3 full factorial design it would require 27 runs with 3 additional zero points for residual error estimation. To visualize a CCD design, it is essentially a 3 level design, but rotated 45 degrees. Figure 3 illustrates this transformation.

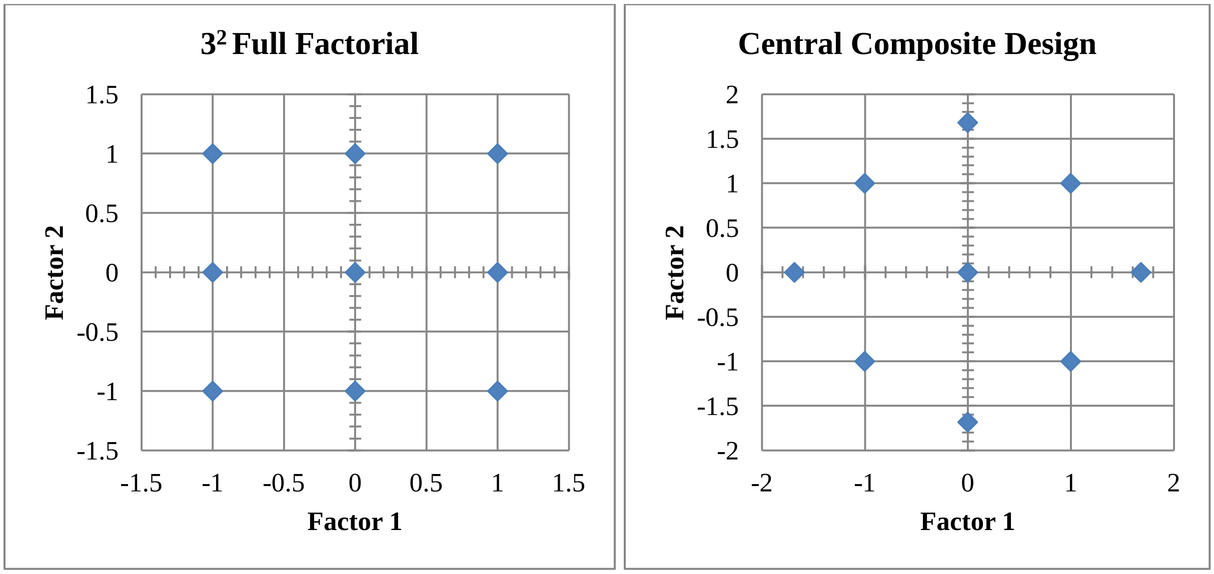

Figure 3. Transformation of 3^2 full factorial design to central composite design by rotating by 45 degrees.

The outlier point is defined by a value called alpha-star. Alpha star is dependent on the number of factors (k) and the fractionalization element (p). The alpha star value is defined, in design units, below in equation 3.

$$alpha - star = 2^{(k-p)/4} \tag{3}$$

3. EXPERIMENTAL PROCEDURE

After the experiment was designed using software package JMP IN, the experiment was carried out over three weeks. The input parameters for the experiment were pre-bake temperature, post-bake temperate and time. The values for the different levels for each input are shown in table 1.

	Pre-bake Temperature (°C)	Post-bake Temperature (°C)	Development Time (Seconds)
- Alpha-star	83	83	33
-1	90	90	40
0	100	100	50
+1	110	110	60
+ Alpha-star	117	117	67

Table 1. Input parameters and the values at which they were set.

The experiment was carried out over three weeks. The first week was primarily to learn and become familiar with the tools required to carry out the experiment. Week two of the experiment, the majority of the

experiment was carried out. And finally the third week any runs that produced unexpected results were reran to confirm that the lithography process was executed correctly. The experiment was carried out using four inch silicon wafers. The wafers were cleaned before any processing was carried out on them. The wafers were coated with HPR 504 positive resist using the SVG track. The wafers were baked pre-exposure using the hot plates, at a temperature specified by the current run. The NanoSpec tool was used to measure the resist thickness. Several points on the wafer were measured in order to get an average initial thickness for the photoresist. The GCA 6700 stepper was then used to expose the wafers with an exposure array of increasing exposure dose. The wafers were then baked again in a post-exposure bake at a temperature defined by the current run. The post-exposure bake was done on the hot-plates as well. The wafers were then developed using CD 26 developer for the amount of time set by the current run. Each die on the wafer was measured using the NanoSpec in order to create the response curve similar to the response curve seen in figure 2.
After the experiment was carried out, the measurements were put into an Excel spreadsheet to perform a least-square regression on the linear part of the graph to get the contrast for each run. The thickness loss and dose to clear were also found for each run using Excel.

4. RESULTS AND ANALYSIS

After all of the desired responses were measured the responses were put in the software package JMP IN. The results put into JMP IN can be found in the appendix. Using the fit model function in JMP IN each response was analyzed one by one. Using a risk-level of 0.05 each insignificant term was removed from the model.
For thickness loss it was found that the pre-bake temperature and development time were the significant factors. This makes sense theoretically for the pre-bake evaporates the solvent and the development time determines for how long the chemical reaction of development takes place. Table 2 shows the parameter estimates for the thickness loss.

Term	Estimate	Std Error	t Ratio	Prob>|t|
Intercept	424.70588	57.14303	7.43	<.0001
prebake(90,110)&RS	-165.0312	63.75473	-2.59	0.0215
time(40,60)&RS	182.97458	63.75473	2.87	0.0124

Table 2. Parameter Estimates for Thickness Loss

Using the parameter estimates and converting from design units to real units the model equation is found for the thickness loss and is described below.

$$Thickness\ loss = 1160.14 - 16.5 * (pre - bake) + 18.3(develop\ time)$$

Table 3 shows the lack of fit for the thickness loss model. It is seen that the p-value of the lack of fit is greater than 0.05, therefore the model is fit.

Source	DF	Sum of Squares	Mean Square	F Ratio
Lack Of Fit	6	469352.81	78225.5	2.0332
Pure Error	8	307794.80	38474.4	**Prob > F**
Total Error	14	777147.61		0.1738
				Max RSq
				0.8084

Table 3. Lack Of Fit for Thickness Loss Model

Table 4 shows the parameter estimates for the dose to clear. It is seen that the pre-bake temperature, post-bake temperature, development time, and the interaction of post-bake and pre-bake temperature are all significant to the dose to clear. Considering that the amount of solvent present in the photoresist affects the PAC sensitivity to light explains the pre-bake temperature being significant. The post-bake evaporates more solvent which would affect the resists sensitivity to the developer. The development time is significant because the development time is directly proportional to the amount of photoresist that will react with the developer. The interaction of the pre-bake and post-bake temperature is significant because they both affect the sensitivity to the exposure light and developer.

Term	Estimate	Std Error	t Ratio	Prob>|t|
Intercept	77.686324	1.49658	51.91	<.0001
prebake(90,110)&RS	10.209838	1.669741	6.11	<.0001
postbake(90,110)&RS	-5.249239	1.669741	-3.14	0.0085
time(40,60)&RS	-4.061148	1.669741	-2.43	0.0316
postbake(90,110)*prebake(90,110)	-6.317813	2.181622	-2.90	0.0134

Table 4. Parameter Estimates for Dose to Clear

Using the parameter estimates and converting from design units to real units the model equation is found for the dose to clear and is described below. Note that pre is simply short for pre-bake temperature, post is short for post-bake temperature and time is short for development time.

$$Dose\ to\ clear = 785.9 - 6.35 * (pre) - 7.90 * (post) - 0.41 * (time) + 0.074(pre * post)$$

Table 5 shows the lack of for the dose to clear model. It is seen that the p-value for the lack of fit is greater than 0.05, therefore the model is fit.

Source	DF	Sum of Squares	Mean Square	F Ratio
Lack Of Fit	10	450.29442	45.0294	13.6143
Pure Error	2	6.61500	3.3075	**Prob > F**
Total Error	12	456.90942		0.0703
				Max RSq
				0.9976

Table 5. Lack Of Fit for Dose to Clear Model

Table 6 shows the parameter estimates for the contrast. It can be seem that the pre-bake temperature, the post-bake temperature, the interaction of the pre-bake temperature and post-bake temperature, and the post-bake squared are all significant. Because the risk level is being set to 0.05, the p-value of 0.0624 would be conventionally removed as not significant. However, if the risk value is increased slightly to 0.063, only an increase of 0.013, the p-value is significant. Therefore the interaction will remain as part of the model for it is very close to the significance level. Theoretically the bake temperatures are the only factors that should affect the contrast of the photoresist. The contrast is mostly a characteristic of the chemical make-up of the photoresist. The bake temperatures affect the chemistry of the photoresist, therefore it makes sense they affect the contrast.

Term	Estimate	Std Error	t Ratio	Prob>|t|
Intercept	1.0879798	0.020148	54.00	<.0001
prebake(90,110)&RS	-0.044754	0.016562	-2.70	0.0192
postbake(90,110)&RS	0.0689611	0.016562	4.16	0.0013
prebake(90,110)*postbake(90,110)	0.0444625	0.02164	2.05	0.0624
postbake(90,110)*postbake(90,110)	-0.051509	0.016957	-3.04	0.0103

Table 6. Parameter Estimates for Contrast

Using the parameter estimates and converting from design unit space to physical units space the following model equation is found. It should be noted that the fact the coefficients and intercept are small simply means that the contrast is not largely variable due to the bake temperatures.

$$Contrast = 0.14 - 0.049 * (pre) - 0.0654 * (post) + 4.45 * 10^{-4} * (pre * post) - 5.15 * 10^{-4}(post^2)$$

Table 7 shows the lack of fit for the contrast model. The p-value for the lack of fit is greater than the significance level of 0.05 therefore the model is significantly fit.

Source	DF	Sum of Squares	Mean Square	F Ratio
Lack Of Fit	4	0.02570974	0.006427	2.6719
Pure Error	8	0.01924458	0.002406	**Prob > F**
Total Error	12	0.04495432		0.1104
				Max RSq
				0.8974

Table 7. Lack Of Fit for Contrast Model

In order to optimize the system the prediction profiler function is ran in JMP IN. In the model it is defined that the contrast is to be maximized while the dose to clear and thickness loss is to be minimized. The prediction profiler uses this information and the model equations to find the input values to maximize and minimize the outputs appropriately. It is seen that if the pre-bake temperature and post-bake temperature are both set to 100 degrees Celsius and the development time is set to 50 seconds that the outputs are maximized and minimized appropriately. If the process is ran at these values, the contrast will be 1.08798, the dose to clear will be 75.47066 mJ/cm^2 and the thickness loss will be 336.86 angstroms. In the prediction profiler the non-linear responses of the variables can be seen.

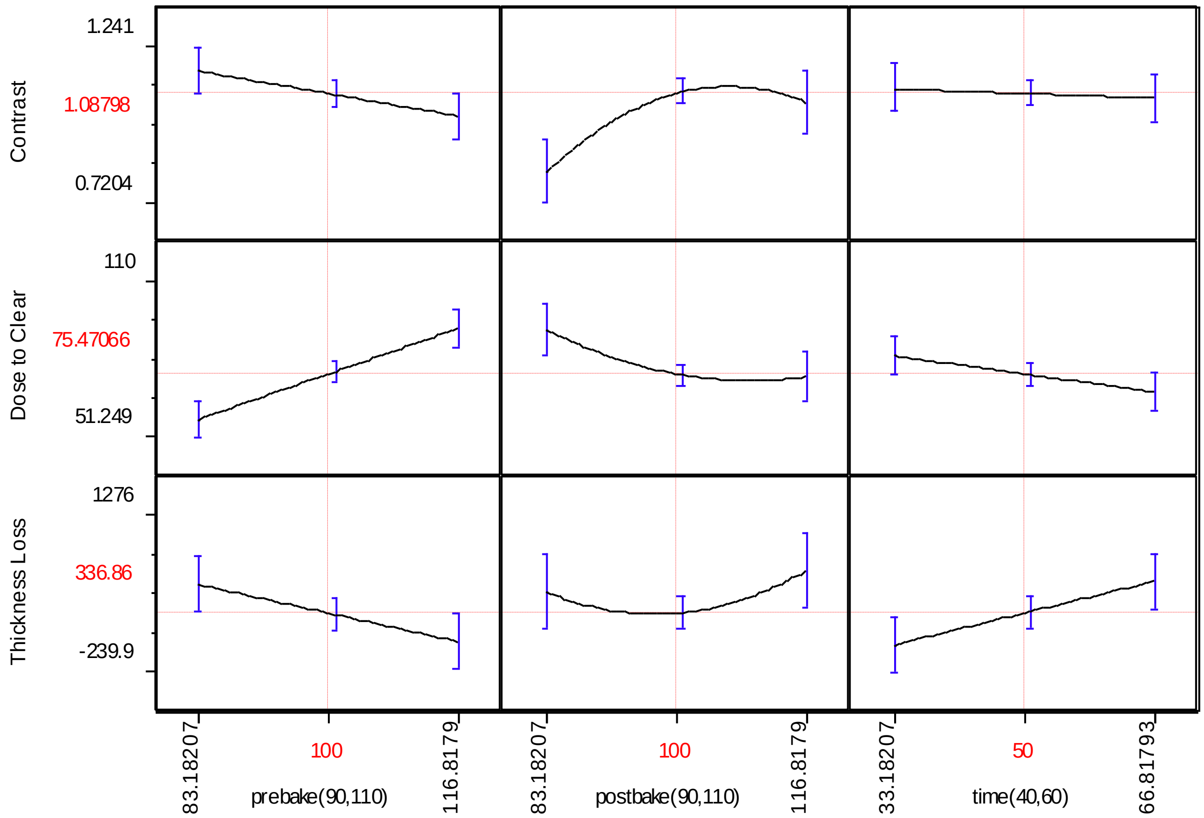

Figure 4. Prediction profiler for the optimization of the all the models.

5. CONCLUSIONS

Through this experiment it was found that the contrast is a function of pre-bake temperature, post-bake temperature, the interaction of pre-bake and post-bake temperatures, and the post-bake temperature squared. The thickness loss was found to be a function of pre-bake temperature and development time. The dose to clear was found to be a function of pre-bake and post-bake temperatures, the development time, and the interaction of pre-bake and post bake temperatures. In order to minimize the thickness loss and dose to clear, and maximize the contrast, the pre-bake temperature and post-bake temperature should be set to 100 degrees Celsius, and the development time should be set to 50 seconds. This will result in a contrast of 1.08798, a dose to clear of 75.47066 mJ/cm^2 and a thickness loss of 336.86 angstroms. Through this experiment it was realized that by using a central composite design it is possible to gain a lot of information about the input parameters in very few runs in comparison to a full 3-level factorial design.

REFERENCES

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[2] S. Wolf, Microchip Manufacturing, Sunset Beach: Lattice Press, 2004.

APPENDIX

Algebra for converting from design units to physical units for main effects. C is a constant, X is an effect.

$$Z = C_0 + C_1 X_1$$

$$Z = C_0 + 2C_1 \frac{X - \bar{X}}{X_{high} - X_{low}}$$

$$Z = C_0 - \frac{2C_1 \bar{X}}{X_{high} - X_{low}} + \frac{2C_1}{X_{high} - X_{low}} X$$

Algebra for converting from design units to physical units for two effect interactions. C is a constant, X and Y are separate effects.

$$Z = C_0 + CXY$$

$$Z = C_0 + C\left[\frac{4(X - \bar{X})(Y - \bar{Y})}{(X_{high} - X_{low})(Y_{high} - Y_{low})}\right]$$

$$Z = C_0 + 4C\left[\frac{XY + \bar{X}\bar{Y} - X\bar{Y} - \bar{X}Y}{X_{high}Y_{high} + X_{low}Y_{low} - X_{low}Y_{high} - X_{high}Y_{low}}\right]$$

Algebra for converting from design units to physical units for a main effect squared. C is a constant, X is an effect.

$$Z = C_0 + CXX$$

$$Z = C_0 + C\left[\frac{2(X - \bar{X})}{(X_{high} - X_{low})}\right]^2$$

$$Z = C_0 + 4C\left[\frac{X^2 + \bar{X}^2 - 2\bar{X}X}{X_{high}{}^2 + X_{low}{}^2 - 2X_{high}X_{low}}\right]$$

Data used in analysis. Negative alpha-star is denoted by a and positive alpha-star is denoted by A.

Pattern	Pre-bake	Post-bake	Development Time	Contrast	Dose To Clear	Thickness Loss
---	90	90	40	1.0738	75.39	211
--+	90	90	60	1.0036	59.8725	1276
-+-	90	110	40	1.1016	72.24	517
-++	90	110	60	0.9969	63.045	940
+--	110	90	40	0.8802	110.04	144
+-+	110	90	60	0.8937	88.425	261
++-	110	110	40	1.1257	78.54	270
+++	110	110	60	1.025	69.405	735
a00	83	100	50	1.166	56.49	503
A00	117	100	50	0.952	94.29	75
0a0	100	83	50	0.8144	91.14	429
0A0	100	117	50	1.1378	78.54	586
00a	100	100	33	1.0987	81.69	107
00A	100	100	67	1.1807	81.69	362
000	100	100	50	1.0949	75.39	304
000	100	100	50	1.0968	72.24	226
000	100	100	50	1.1504	72.24	274