Characterization of a non-chemically amplified resist for photomask fabrication using a 257 nm optical pattern generator

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ABSTRACT

I-line optical pattern generators using non-chemically amplified resists have become the workhorses for high throughput mask fabrication. The demand for smaller and more uniform features on photomasks has driven the development of a 257 nm optical pattern generator. A non-chemically amplified resist is being developed to maximize the performance of this new 257 nm mask tool. Resist characterization and lithography simulation are being used to formulate a non-chemically amplified resist for 257 nm optical pattern generators.

Non-chemically amplified resists are advantageous for us in mask fabrication due to their storage and post-exposure stability. Chemically amplified resists may provide higher performance but they also require environmental mini-environments and a post-exposure bake equipment not commonly present in mask houses. Diazonaphthoquinone (DNQ)/ novolak resists have not been used for DUV Integrated Circuit (IC) applications mainly due to the low sensitivity and the strong absorbance of the DNQ photoactive compound (PAC) at 248 nm. However, a 2,1,4 DNQ based resist has been characterized that bleaches at 257 nm and inhibits novolak. The photoproduct of the 2,1,4 DNQ PAC is much more transparent at 257 nm than 248 nm. Novolak resin is too strongly absorbing for use in formulating efficient 248 nm resists, but novolak has an absorbance minimum at 257 nm that provides transparency similar to poly (hydroxystyrene).

Lithography simulation is being used to develop a non-chemically amplified resist to minimize the expensive iteration of manufacturing trials. An exposure system using a 257 nm frequency doubled Ar laser system has been constructed to study the resist photokinetics. Dill exposure parameters (*A*, *B* and *C*) have been extracted for a 2,1,4 DNQ/ novolak based resist. Dissolution rate measurements have been made with a DRM developed at the University of Texas at Austin. Simulation is used to determine the optimal resist absorption, bleaching, dose and dissolution properties to maximize resolution. It is possible to formulate a high performance resist for 257nm if care is taken in optimization of the formulation.

Keywords: DUV non-chemically amplified photoresist, lithography simulation and photomask

1. INTRODUCTION

The fabrication of photomasks with smaller and more uniform linewidths is critical for the development of phase-shifting and optical proximity correction features and improvements in the control of CD error are required even for 0.25 μ m ground rule masks [1]. The extension of DUV lithography through implementation of resolution enhancements like phase shifting and OPC requires further reduction in the mask critical-dimension error [2]. The development of a non-chemically amplified resist process for a 257 nm optical pattern generator is an important step toward achieving these improvements.

Non-chemically amplified resists have not been used for DUV lithography applications due to the high absorbance of novolak resins and the lack of bleaching photoactive compounds at 248 nm. Fortunately, novolak resins have much higher transparency at 257 nm than at 248 nm. DNQ photoactive compounds also bleach more at 257 nm than 248 nm. The location of the substituent group on the DNQ PACs affect the level of bleaching and the ability of the PAC to inhibit the dissolution of novolak. The majority of I-line resists have been developed with ballast groups linked as sulfonate esters on the 5 position of the diazonaphthoquinone. However, the isomeric DNQ PACs with the sulfonate substituent attached at the 4 position (2,1,4 DNQ) provide more bleaching at 257 nm. A multi-functional 2,1,4 DNQ that strongly inhibits the

dissolution of novolak has been provided by the Shipley Company. We have formulated resists with the 2,1,4 DNQ that maximize dissolution contrast.

Resist characterization and lithography simulation are being utilized to rationally formulate the resist. Resist characterization has been used to optimize the optical transparency, extent of PAC bleaching, PAC photospeed and dissolution contrast performance tradeoffs. The main challenge in formulating a DUV non chemically amplified resist is to understand the effects of higher novolak and PAC photoproduct optical absorption on resist profiles. Formulations of the 2,1,4 DNQ based resists have been characterized by extracting exposure (Dill's *A*, *B* and *C*) and development rate (R(m)) parameters. Optical properties have also been measured independently for absorption of the PAC, PAC photoproduct and resin at 257 nm. The exposure and development rate parameters were extracted from experiments on AR3 coated photomask substrates using a post-exposure bake. The characterization of the 2,1,4 DNQ PAC in a novolak resin demonstrates that these resist materials have acceptable bleaching and dissolution inhibition properties for the formulation of a non-chemically amplified resist for 257 nm mask optical pattern generators.

2. THEORETICAL

2.1 Rational chemical design of a DUV non-chemically amplified resist

I-line resists have utilized 2,1,5 DNQ PACs predominantly due to their good bleaching and novolak dissolution inhibition properties. However, the 2,1,4 DNQ bleaches more at 257 nm than the 2,1,5 DNQ [3]. The difference in the PAC structures is in the attachment of the sulfonate substituent. The general structures are shown in Figures 1 and 2.



Figures 1: 2,1,4 DNQ

Figure 2: 2,1,5 DNQ

Multifunctional PACs are those that contain multiple PAC moieties attached to a single ballast group. Trefonas and Daniels [4] with additional work from Trefonas and Mack [5] have shown how the dissolution contrast (change in dissolution rate with dose) and the resulting resist sidewall angles increase with the number of PAC moieties (up to 6 DNQs) attached to a ballast group. However, an increase in the number of photoactive substituents increases the exposure dose and base concentration required for development. Tri-functional PACs are often used as a compromise between dissolution contrast, dose and developer concentration.

Dammel [6] and Szmanda et al [7] have shown that increases in the distance (hydrophobicity) between the multiple DNQ moieties on the ballast group improve the dissolution inhibition of novolak. Dammel describes the higher dissolution inhibition efficiency for the PACs through a chromophore proximity effect that blocks the phenolic sites on the novolak. An example of a difunctional PAC that exhibits strong dissolution inhibition (0.12 A/sec in 0.331N TMAH) through this proximity effect is shown in Figure 3 [8].



Figure 3: Inhibitor proximity effect for dissolution inhibition by a multifunctional DNQ

The mechanism for dissolution inhibition of novolak with multiple DNQ PACs can be described through the critical ionization model [9]. The model proposes that the dissolution rate is proportional to the fraction of ionized to un-ionized sites (phenolic) in the novolak resin. The sulfonate functional groups on the unexposed DNQ moieties provides hydrogen bonding to the phenolic hydroxyl groups on the novolak resin. The hydrogen bonding increases the dissolution inhibition of novolak by effectively decreasing the "effective pK_a" of the novolak polymer. A tri-functional 2,1,4 DNQ PAC supplied by Shipley has demonstrated strong dissolution inhibition, excellent bleaching at 257 nm.

Highly inhibiting novolak resins have been sought to provide a large dissolution contrast with minimal concentration of multifunctional 2,1,4 DNQ PAC. Novolak has an absorption minimum close to 257 nm that is similar to that of poly(hydroxystyrene). The novolak resin supplied by the Shipley Company has the following structural form where the substituent R_1 , R_2 and R_3 represent H, alkyl and alkoxide functional groups (Figure 4). The novolak structure takes advantage of the ortho-ortho linkages between the cresol monomers to provide strong dissolution inhibition [9].



Figure 4: Novolak polymer

2.2 Application of Dill's equations to resists with absorbing photoproducts

The novolak resin and photoproducts of non-chemically amplified resists absorb more in the DUV than at I-line exposure wavelengths. The influence of the absorption of the resin and photoproducts are quantified through analysis with Dill's exposure equations [10]. Dill's equations describe the resist absorbance as a single sum of the absorption of the PAC (m), photoproduct (p), resin (r) and solvent (s).

$$\boldsymbol{a} = a_m[M] + a_p[P] + a_r[R] + a_s[S] \tag{1}$$

 a_m , a_p , a_r and a_s is the molar absorption coefficient of each species [M], [P], [R] and [S] are the molar concentration of each species

Dill simplifies this general absorption equation in terms of a bleachable component (A), the relative PAC concentration (m) and a non-bleachable component (B).

$$\boldsymbol{a} = A\boldsymbol{m} + \boldsymbol{B} \tag{2}$$

where

$$\begin{split} A &= (a_m \text{-} a_p)[M]_o \\ [M]_o &= \text{initial concentration of PAC} \\ m &= [M]/[M]_o \\ B &= a_r[R] + a_p[M]_o + a_s[S] \end{split}$$

Dill's simplified equations can be reorganized to separate out the influence of the absorption of each component, especially the absorption of the PAC and photoproduct (Equations 3 and 4).

$$\mathbf{a} = a_m[M]_o m + a_p[M]_o(1-m) + a_r[R] + a_s[S]$$
(3)

$$\boldsymbol{a} = A_2 \boldsymbol{m} + B_p (1 - \boldsymbol{m}) + B_r \tag{4}$$

where

$A_2 = a_m[M]_o$	(PAC absorption)
$B_p = a_p[M]_o$	(photoproduct absorption)
$B_r = a_r[R] + a_s[S]$	(resin and solvent absorption)

The absorption of the individual species in the 2,1,4 DNQ resists as a function of PAC concentration have been measured with an ellipsometer to optimize the resist absorption while taking into account the change of index of refraction as shown in Equations 5 and 6 where k_1 and k_2 are the complex indices of refraction of the films at the wavelength λ .

$$A = \frac{4\mathbf{p}(k_2 - k_1)}{\mathbf{l}} \tag{5}$$

$$B = \frac{4\mathbf{p}k_1}{\mathbf{l}} \tag{6}$$

Dill's exposure rate parameter, C, can be calculated using A and B parameters measured with an ellipsometer and the initial slope of the bleaching curves from each resist (Equation 7). Calculation of C using this method does not take into account the variation of PAC concentration due to standing waves during bleaching. However, this simple method provides good estimates for screening resist materials.

$$C = \left(\frac{A+B}{A}\right) \left(\frac{1}{T(0)\{1-T(0)\}}\right) \left(\frac{dT(0)}{I_0 dt}\right) = \left(\frac{A_2 + B_r}{A_2 - B_p}\right) \left(\frac{1}{T(0)\{1-T(0)\}}\right) \left(\frac{dT(0)}{I_0 dt}\right)$$
(7)

where

T(0) is the initial transmittance $I_0 =$ Initial transmittance

2.3 Dissolution Rate Measurements

Dissolution rate measurements are used to quantify the inhibitor strength and dissolution contrast of the resist. Dissolution inhibition (Rmin) as a function of PAC concentration (Meyerhoffer plot) determines the level of PAC that is necessary to adjust resist loss in an unexposed film. Our goal is to determine the level of PAC necessary to minimize resist loss while maximizing the contrast (Rmax/Rmin) by utilizing strongly inhibiting PAC/ novolak combinations.

Resist modeling requires the measurement of the dissolution rate as a function of film thickness and dose (R(m)). This data is then fit to a dissolution rate model. Modern, high-resolution photoresists have a "notch" behavior characterized by a sharp increase in development rate at a critical normalized photoactive-compound concentration [11]. Dissolution rate models can be utilized to determine the optimal developer concentration that provides a sharp increase in development at the target nominal feature size.

2.4 Exposure and dissolution parameter optimization utilizing the lithographic imaging equation

The optimal resist development response occurs when the resist completely dissolves with perpendicular sidewalls while maintaining the nominal linewidth. A sharp or notch development response depends on the strength of inhibition between the PAC and novolak resin, the molecular weight distribution of the resin and the developer concentration. A strongly inhibiting PAC and narrow resin molecular weight distribution has been found to increase dissolution contrast and the resulting resolution [12]. The developer concentration is adjusted to provide development at the appropriate relative PAC concentration located at the target linewidth.

The influence of both the exposure and dissolution properties of the resist can be quantified mathematically through the use of "line-edge optimization" with the lithographic imaging equation. The relative PAC concentration (*m*) can be calculated in any volume element in the film. The m is calculated by convolving the aerial image and the resist exposure parameters. A change in PAC concentration through the horizontal position in the resist defines a relative PAC gradient ($\tilde{N}n$) at the nominal feature edge. An optimal exposure dose exists that maximizes $\tilde{N}n$ at the nominal resist feature edge. The optimum process

latitude is achieved when the maximum $\tilde{N}n$ and the maximum resist contrast (g_i) occur at the same relative PAC concentration (m^*) , and that concentration is located at the edge of the resist feature (x^*) where *R* is the dissolution rate of the resist and *x* is the horizontal direction parallel to the substrate. (Equations 8 and 9).

$$\frac{\partial R}{\partial x}\Big|_{x^*} = \mathbf{g} \frac{\partial m}{\partial x} \qquad \nabla m = \frac{\partial m}{\partial x} \qquad (8)$$
$$\mathbf{g}_R(m^*) = \frac{dR}{dm} \qquad (9)$$

The resist contrast can be maximized at x^* by adjusting the developer concentration. It should be noted that one consequence of maximizing the contrast of a resist is the amplification of influence of standing wave phenomena.

2.4 Resolution and DOF Considerations

The driving force for development of a 257 nm optical pattern generator is gain in resolution by using a lower wavelength of light (Equation 10). The resolution equation is dependent on the wavelength of light, NA of the lens system and the k factor. The k factor depends upon the image and resist dissolution contrast (lithographic imaging equation).

$$R = k_1 \frac{\mathbf{I}}{NA} \tag{10}$$

The DOF is proportional to the wavelength and inversely proportional to the square of the NA. Thus, increases in resolution has the tradeoff of loss in depth of focus. The Rayleigh limit for depth of focus in an IC process is based on a k_2 value of 0.5. An estimate of the DOF using an NA of 0.8 and a k_2 of +/-0.5 reveals that the total DOF is 570 nm for I-line and 400 nm for 257 nm.

$$DOF = \pm k_2 \frac{\mathbf{I}}{NA^2} \tag{11}$$

2.5 Organic Antireflection Coatings for 257 nm Optical Pattern Generators

High resolution I-line mask processes resolve standing waves that result from small reflections from the chromium oxide/ chromium film stack [13]. Organic antireflective coatings can be used to minimize reflections and remove standing waves while minimizing the swing ratio of the resist swing curve. The use of organic antireflection coatings for 257 nm optical pattern generators opens the possibility of a high resolution non-chemically amplified resist process without the necessity of a post-exposure bake. An accompanying paper describes the use of organic antireflection coatings for photomask processes [14].

3. EXPERIMENTAL

3.1 Laser exposure system (257 nm)

An exposure system based on a Coherent frequency doubled (FreD) argon ion laser exposure system has been developed to study the photokinetics and dissolution properties of resist components at 257 nm. The Sabre FreD laser is the same laser intended for the full-scale 257 nm optical pattern generator. Expansion and collimating optics have been designed to provide uniform exposure intensity incident on the resist. A uniform intensity profile is created by sending the light through a 1 mm diameter aperture (pin hole) to spatially filter the gaussian-shaped laser beam. The pin-hole cuts out a small portion of the expanded beam to create a uniform intensity. The spatial coherence of the beam is destroyed with a fused silica spinning diffuser to remove speckle and diffraction patterns from the pin-hole. The beam is finally expanded to around 8 mm in diameter for exposure of resist located on a vertical stage. The stage is designed to hold 4 inch diameter AR3 coated mask substrates and 4 inch diameter transparent quartz substrates. A PM3 Molectron thermopile power meter is used to measure

the intensity of the beam. The uniformity of the exposure intensity has been indicated through uniform development rates over the exposure area in the resist.



Figure 5: Laser Exposure System (257 nm) for Photoresist Characterization

3.2 Photoresist Coating and Baking Conditions

Photoresist formulations were spin coated at a thickness of approximately 375 nm on 4 in. diameter thick AR3 coated quartz disks from Hoya Corp using a PWM32 Headway spinner. A hotplate was built that mimics the post-application bake temperature-time profile of the surface of a mask blank subject to the PAB cycle at a commercial coating facility. The hotplate incorporates a gain scheduled temperature control system that heats the thinner substrate surface to a temperature vs. time profile that matches that of the thicker commercial substrate. The PAB consisted of a 5 minute temperature-time trajectory bake that approaches 90 °C at the surface of the mask. The PAB requires around 3 minutes for the surface of the mask to reach a steady state temperature around 90 °C and the final 2 minutes to bake the non-chemically amplified resist. The photoresist films used in collecting R(m) data required a post-exposure bake to remove standing waves in the DRM data. The post-exposure bake consisted of a 5 minute bake that ramped up to 110 °C. Resist films that have a PAB hotter than 90 °C have higher glass transition temperatures that require a hotter post-exposure bake (120 °C) to effectively diffuse the PAC and remove standing waves.

4. RESULTS

The formulation of a non-chemically amplified 257 nm resist is based on balancing the transparency, bleaching, dissolution inhibition and dissolution promotion properties. Resist characterization is used to screen resist materials supplied from multiple resist vendors. Simulation is used to balance the performance tradeoffs and thus, maximize the resist resolution.

4.1 Bleaching characteristics of a 2,1,4 DNQ photoactive compound

A trifunctional 2,1,4 DNQ photoactive compound supplied by Shipley bleaches at 257 nm (Figures 6 and 7). The bleaching experiments were performed by measuring the absorbance of unexposed and exposed photoactive compound solutions in acetonitrile. The absorbance of the solution was measured as a function of wavelength to determine the level of bleaching that occurs at 257 nm. The 2,1,4 DNQ bleaches more than the 2,1,5 DNQ PACs at 257 nm. The 2,1,4 DNQ bleaches from a level of 1.0 AU to around 0.25 AU and the 2,1,5 DNQ bleaches from 1.7 AU to 0.5 AU with broadband exposure. Both PACs bleach a lot more at 257 nm than 248 nm.



4.2 Transparency of novolak versus poly(hydroxystyrene) based resists at 257 nm

The novolak resin has transparency similar to poly(hydroxystyrene) at 257 nm (Figure 8). The absorbance of novolak and PHS was measured with a UV-VIS spectrometer. Novolak is the ideal resin to formulate a non-chemically amplified resist at 257 nm due to its similar transparency to poly(hydroxystyrene) and its stronger inhibition properties with DNQ PACs.



Figure 8: Novolak has similar optical properties to PHS at 257 nm

4.3 Dissolution inhibition of novolak with 2,1,4 DNQ and diazocoumarin PACs

The dissolution inhibition and promotion of novolak with a trifunctional 2,1,4 DNQ was studied using a 0.26N TMAH developer (TOK NMD-W surfactant). The 2,1,4 DNQ PAC was found to have a strong inhibition effect on the novolak dissolution (Figure 9). The novolak resin has a dissolution rate around 12 nm/sec without a photoactive compound. The DNQ PAC inhibited the dissolution rate of novolak down to 0.17 nm/sec at a concentration of 0.1 molal (moles of PAC/ kg of polymer) and 0.03 nm/sec at a concentration of 0.15 molal. We have chosen to simulate the 0.1 molal 2,1,4 DNQ that demonstrates the lowest amount of PAC needed to minimize resist loss. The dissolution contrast indicated through a crude

Rmax (exposed)/ Rmin (unexposed) analysis increases exponentially with PAC concentration. The Rmax/Rmin was 94 for the 0.1 molal DNQ resist versus 505 for the 0.15 molal DNQ resist.



Figure 9: Meyerhoffer plot showing the dissolution properties of DNQ in novolak resin

The trifunctional 2,1,4 DNQ appears to be a strong inhibitor due to the higher functionality and backbone. The ideal backbone for DNQ based PACs is a large hydrophobic backbone that increases the proximity effect of the multiple PAC increased dissolution inhibition [6].

4.4 Dill Exposure Parameters for non-chemically amplified resists with absorbing photoproducts

Improved dissolution inhibition and contrast occurs with higher PAC concentration at the expense of higher absorption by the PAC and photoproduct at 257 nm. Our goal is to develop a process that operates at exposure doses under 200 mJ/cm², the dose specification set by the mask tool vendor. Furthermore, we seek to maximize the sidewall angle or resolution of the resist by minimizing photoproduct absorption (Dill's B parameter). The absorption of the 2,1,4 DNQ resist components was measured as a function of PAC concentration to determine Dill's A and B values used in simulation (Table 1). The individual absorption of the PAC (A₂), resin (B_r) and photoproduct (B_p) was also measured to determine the relative contribution of the resin and photoproduct absorption in an exposed resist. The optimum resist formulation maximizes the extent of PAC bleaching (A₂) while minimizing photoproduct ratios (A₂/ B_p) ratios of 2.7 and 2.3, respectively. The most transparent resist is the 0.10 m DNQ resist that has a Dill A value of 0.81 1/micron and B value of 1.55 1/micron.

	A (1/ mm)	B (1/mm)	$B_r(1/mn)$	$B_n(1/mn)$	A, (1/ mm)	C (cm ² /mJ)	Absorbance (B _n /B %)
CA resist	0.00	0.94	0.94	0.00	0.00		0
Novolak only	0.00	0.94	0.94	0.00	0.00		0
0.10 m DNQ	0.81	1.55	0.94	0.61	1.42	0.04	39
0.15 m DNO	1.28	1.70	0.94	0.76	2.04	0.03	45

Table 1: Absorption of 2,1,4 DNQ as a function of PAC concentration at 257 nm

It must be noted that the absorbance of these resists is still higher than typical I-line resists like IP3600 (TOK) that has a Dill A value of $0.86 \ \mu m^{-1}$, B value of $0.10 \ \mu m^{-1}$ and a C value of $0.014 \ cm^2/mJ$. Simulation is needed to quantify the effects of a higher resin and photoproduct absorbance on the resist sidewall profiles. It has also been determined that the photoproduct contributes 39% while the resin contributes 61% of the total absorption for a fully exposed 0.1 m DNQ resist in novolak. The only way to decrease the absorption of the resist is to find another novolak resin that can be more strongly inhibited with a 2,1,4 DNQ PAC concentration below 0.1 molal or develop a PAC that has more transparent photoproducts. A graph of Dill's A and B values as a function of DNQ PAC concentration is shown in Figure 10.



Figure 10: Dill's A and B values (absorption) as a function of PAC concentration at 257 nm

Dill's exposure rate parameter, C, was measured for the DNQ based resists in the novolak resin (Figure 11). The C parameter was determined experimentally from the bleaching curves that reveal the change in the transmittance of the resist with exposure dose at 257 nm. The transmittance measurements were made on approximately 375 nm resist films exposed to incremental amounts of 257 nm light and analyzed with an UV-VIS at 257 nm.



Figure 11: Bleaching Curve for 2,1,4 DNQ at 0.1 and 0.15 molal

The exposure rate constant (C) was calculated using Dill's equations while the A and B values were extracted using ellipsometry to take into account the changes in index of refraction. The C equation also required measurement of the initial transmittance and the initial change in transmittance with dose from the bleaching curves in Figure 11. The C values were calculated for the 2,1,4 DNQ at both the 0.1 molal and 0.15 molal concentration are 0.043 cm²/mJ and 0.031 cm²/mJ, respectively. The high photospeed is ideal for a non-chemically amplified resist at 257 nm to keep the dose to size below 200 mJ/cm². However, the exposure rate constant appears to be much higher than 0.01 cm²/mJ at I-line. The trifuntional 2,1,4 DNQ may have a higher quantum efficiency at 257 nm than standard I-line PACs. More experiments are necessary to confirm the exposure rate constants.

4.5 Optimal Image Transfer for High Resolution Imaging

The exposure dose that maximizes the DOF for each resist system can be determined by modeling the image transfer into a bleaching resist. Simulation of the aerial image of a 350 nm space at various focus positions from a 257 nm pattern generator is shown in Figure 12. The best process latitude occurs when the conjugate point in the image is located at the edge of the nominal resist feature. The conjugate point in the aerial image occurs at a specific feature size where the relative intensity is constant through focus. The dose that images the resist with this conjugate point is the isofocal dose.



Figure 12: Simulated Image of a 0.35 micron Space revealing the image conjugate points

The aerial image from the mask writer is transferred into the resist film through exposure of the photoactive compound. The exposed PAC profile creates a photoactive compound distribution in the resist from low concentration of PAC in the high dose region of the resist feature (center) to the high PAC concentration at the low dose region of the resist. Our goal is to determine the exposure dose that maximizes this PAC gradient at the feature edge. The optimal dose was simulated to be lower (138 mJ/cm²) for the lower PAC concentration of 0.1 molal versus 225 mJ/cm² for the 0.15 molal DNQ/ novolak resists. A simulation of the PAC gradient at the bottom edge of the resist as a function of exposure dose is shown in Figure 13.



Figure 13: Optimal Exposure Dose to Maximize the PAC Gradient is a Function of PAC Concentration

The dissolution threshold can now be adjusted to occur at the simulated PAC concentration where the sharpest PAC gradient occurs at the edge of the resist feature. Simulation is used to determine the relative PAC concentration where dissolution needs to occur to meet the target feature size. Simulation reveals that dissolution of the resist needs to occur at a relative PAC concentration around 0.3 to meet the target feature size at best dose(Figure 14). Optimal image transfer occurs when the dissolution threshold is located at the PAC concentration in the resist resulting from the dose giving in the maximum PAC

gradient. With too weak or too strong a developer the processes would need to be over or under dosed relative to the optimum to meet the target feature size.



Figure 14: PAC Distribution with the optimal Exposure Dose in the 0.1 molal 2,1,4 DNQ/ Novolak resist

4.6 Dissolution Modeling and Parameter Extraction

The dissolution threshold as a function of developer concentration can be determined through an R(m) analysis. The dissolution rate of photoresists was measured using a development rate monitor (DRM) developed at the University of Texas at Austin [15,16,17]. Dissolution rate measurements are made as a function of resist thickness on the 4 in. diameter AR3 coated photomask substrates. The resist films are post-exposure baked to remove standing waves or oscillating changes in dissolution rate as a function of film thickness. An R(m) was extracted for the 0.1 molal 2,1,4 DNQ/ novolak resist with a developer concentration of 0.26N TMAH (TOK NMD-W) using software developed at the University of Texas at Austin. The R(m) curve reveals that dissolution initiates at a relative PAC concentration of 0.7 with this developer (Figure 15). The dissolution threshold needs to occur at a PAC concentration of 0.3. A lower developer concentration is needed to maximize the process latitude and resolution, and is recommended for initial manufacturing trials.



Figure 15: Dissolution Rate as a Function of PAC Concentration

4.7 Simulation of a DNQ/ Novolak resist using a 257 nm laser mask writer

Simulation reveals that we can successfully image a non-chemically amplified for 257 nm mask lithography (Figure 16). The simulation has been done of a 3D UT (PROLITH 3D 6.05) structure using our generated aerial images, exposure parameters and dissolution rate models. The resist was 440 nm thick processed with a PAB of 90 °C for 300 seconds and no PEB. Simulation reveals that small standing waves exist in the film. Standing waves can be removed using an organic ARC or post-exposure bake. This simulation reveals that a potential NCA resist process exists for the 257 nm laser writer. Manufacturing trials are now needed to confirm the simulated profiles.



Figure 16: Simulation of a 3-D 0.35 micron space in a 0.1 molal 2,1,4 DNQ/ novolak resist

5. CONCLUSIONS

Simulation and resist characterization has been done to demonstrate that a non-chemically amplified resist can be used for 257 nm mask lithography. A trifunctional 2,1,4 DNQ PAC exists that strongly bleaches and inhibits novolak at 257 nm. The NCA resist is formulated with the lowest amount of PAC that will minimize resist loss while maximizing transparency at 257 nm. Analysis with Dill's exposure parameters reveals that the 2,1,4 DNQ (0.10 molal)/ novolak resist has a high enough photospeed to exposure resist features with less than 200 mJ/cm². Line edge optimization is also being done to determine the developer concentration that maximizes the resolution and DOF. The resist process can be improved through the removal of standing waves using a organic antireflective coating and/ or a post-exposure bake.

Resist characterization reveals that chemically amplified resists are much more transparent at 257 nm than the DNQ/ novolak resists. Higher transparency provides better image transfer that results in steeper sidewall angles and wider process latitudes. Research is necessary to determine whether the post-coat and exposure stability of CA resists is adequate for mask making. Infrastructure changes like a post-exposure bake and cluster tools with minienviroments needs to be evaluated for the mask industry. Ultimately, this infrastructure will provide the mask industry with a high resolution and high throughput mask fabrication process to meet future photomask specifications. Until that capablity is in place, this NCA resist can be used successfully.

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7. **REFERENCES**

- 1. Kuijten, J. P.; Duray, F.; Kinderen T. D., "Analysis of Reticle Contributions to CD Uniformity for 0.25 μm DUV Lithography," *Proc. SPIE-Int. Soc. Eng.* **1998**, *3334*, 620-628.
- 2. Wong, A. F.; Ferguson, R.A.; Liebmann, L. W.; Mansfield, S. M.; Molless, A. F.; Neisser, M. O., "Lithographic Effects of Mask Critical Dimension Error," *Proc. SPIE-Int. Soc. Eng.* **1998**, *3334*, 106-116.
- 3. Thompson, L. F., Willson, C. G., Bowden, M. J., *Introduction to Microlithography*, Second Edition, American Chemical Society, Washington, DC, **1994**, 171-172.
- 4. Trefonas, P., Daniels, B. K., Proc. SPIE-Int. Soc. Eng. 1987, 194, 476-482.
- 5. Trefonas, P., Daniels, B. K., Proc. SPIE-Int. Soc. Eng. 1991, 1466, 117-131.
- 6. Dammel, R., Diazonaphthoquinone-based Resists, SPIE Optical Engineering Press, volume TT 11, 1993, 90.
- 7. Szmanda, C. R., Zampini, A., Madoux, D. C., McCants, C.L., Proc. SPIE-Int. Soc. Eng. 1989, 1086, 363.
- 8. Uenishi, K., Kawabe, Y., Kokubo, T., Slater, S., Blakeney, A., Proc. SPIE-Int. Soc. Eng. 1991, 1466, 102-116.
- McAdams, C. L.; Flanagin, L. W.; Henderson, C. L.; Pawloski, A. R.; Tsiartas, P.; Willson, C. G., "The Dissolution of Phenolic Polymers in Aqueous Base: The Influence of Polymer Structure," *Proc. SPIE-Int. Soc. Eng.* 1998, 3333, 1171 -1179.
- Dill, F. H.; Hornberger, W. P., Hauge; P. S.; Shaw, J.M., "Characterization of Positive Photoresists," *IEEE Trans. Electron Devices* 1975, 22(4), 445-452.
- 11. Arthur, G.; Mack, C. A.; Martin, B., "A New Development Model for Lithography Simulation," Olin Microlithography Seminar, Interface '97 November 1997, 55-56.
- 12. Yu, J. J.; Meister, C. C.; Vizvary, G.; Xu, C-B.; Fallon, P., "Sub-0.30 μm I-line Photoresist: Formulation Strategy and Lithographic Characterization," *Proc. SPIE-Int. Soc. Eng.* **1998**, *3333*, 1365-1380.
- Rathsack, B. M., Tabery, C. E., Scheer, S. A., Willson, C. G., Univ. of Texas/ Austin, Henderson, C. L., Georgia Institute of Technology, Pochkowski, M., ETEC Systems, Inc., Philbin, C., Reticle Technology Center (DPI) and Buck, P. D. Dupont Photomask, *Photoresist optimization and process simulation for laser photomask microlithography*, *Proc. SPIE-Int. Soc. Eng.*, 1999, 1215-1226.
- 14. Rathsack, B. M., Tabery, C. E., Philbin, Pochkowski, M., Willson, C. G., "Organic Antireflection Coatings for Photomask Fabrication using Optical Pattern Generators," *Photomask Technolocy and Management*, 1999, 3873-48.
- 15. Henderson, C. L.; Pancholi, S. N.; Chowdury, S. A.; Willson, C. G.; Dammel, R. R., "Photoresist Characterization for Lithography Simulation Part 2: Exposure Parameter Measurements," *Proc. SPIE-Int. Soc. Eng.* 1997, 3049, 816 828.
- Henderson, C. L.; Tsiartas, P. C.; Pancholi; S. N. Chowdury, S. A.; Dombrowski, K. D.; Willson, C. G.; Dammel, R. R., "Photoresist Characterization for Lithography Simulation Part 3: Development Parameters Measurements," *Proc. SPIE-Int. Soc. Eng.* 1997, 3049, 805 - 815.
- Henderson, C. L.; Scheer, S. A.; Tsiartas, P. C.; Rathsack, B. M.; Sagan, J. P.; Dammel, R. R.; Erdmann, A.; Willson, C. G., "Modeling Parameter Extraction for DNQ-novolak Thick Film Resists," *Proc. SPIE-Int. Soc. Eng.* 1998, 3333, 256-267.