A New Materials-based Pitch Division Technique

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Several techniques have been proposed to achieve higher resolution from 193 nm optical lithography [1]. Most of these techniques require the design of new exposure tools or implementation of costly extra process steps. A new pitch division technique is reported, which doubles the resolution of conventional lithography tools by simply adding one component to the photoresist formulation. This technique creates a resist system that involves a series of linked photochemical reactions (A→B→C) in which a photoacid generator (PAG) produces an intermediate species (B) that is a strong acid, which in turn undergoes a reaction that produces a neutral and inert compound (C) that is the final product. The intermediate acid concentration is low at lower doses, but it is largely consumed at higher doses. At moderate doses, the acid concentration reaches its maximum. This property could, in principle, be exploited to double the frequency of a grating on a mask. One formulation that provides this sort of resist response incorporates both a photoacid generator and a photobase generator. This system was studied by simulation and a test formulation was demonstrated to produce the expected resist response.

Keywords: pitch division, frequency doubling, photobase generator, dual tone response

1. Introduction

The drive to sustain the productivity improvements that derive from following Moore’s law has led the semiconductor industry to explore new technologies that enable production of patterns in resist at sub-30 nm half pitch resolution. Immersion lithography successfully enabled printing at 45 nm half pitch, but attempts to extend this technology by use of high index fluids and new lens materials have been abandoned. Hence, new patterning processes were developed, such as double patterning lithography (DPL), which has demonstrated sub-30 nm half pitch resolution. Unfortunately, DPL requires more masks and several added processing steps for each patterned layer and it creates a serious alignment and overlay challenge [2]. This alignment issue could be eliminated by double exposure lithography (DEL) since this process leaves the wafer on the chuck between two exposure passes [3]. Feasible photochemical systems have been proposed and simulated for DEL and the material development is still in progress [4-7]. Continued work in this area is clearly warranted.

Other resolution improvement techniques, such as side-wall deposition and dual-tone development, are being evaluated, which focus on pitch division and require only a single exposure [8-11]. The side-wall deposition approach demonstrates excellent critical dimension (CD) control. However, this approach requires extra processing steps outside the exposure tool, which increase processing cost. The dual-tone development approach exploits the change in resist polarity that occurs after a post exposure bake (PEB). In this scheme, both positive and
negative tone developers are employed to enable pitch division in the resist. Gratings with 64 nm line widths have been demonstrated using this method.

In 2000, IBM patented a dual-tone “hybrid” photoresist composition [12] for 248nm exposure. In this system, the unexposed resist is insoluble and heavily exposed resist is insoluble due to crosslinking, but areas of the resist that receive an intermediate dose are soluble. This sort of response produces pitch division as shown in Fig. 1. Recently, a system based on this same design concept was described by MIT Lincoln Labs[13].

In both the MIT and IBM systems, the negative tone pattern is achieved by crosslinking, which produces an insoluble network at high exposure doses. Historically, negative tone imaging systems based on crosslinking have had resolution limitations due to swelling distortions that occur during development. Never the less, both of these systems are impressive demonstrations of creativity and achieve pitch division from a single exposure.

A new way to achieve pitch division with a single exposure is proposed that does not require crosslinking chemistry, the design of new polymers or any change in the development process. This can be accomplished if it is possible to create a resist response, i.e. acid concentration profile, which has twice the frequency of the aerial image as illustrated in Fig. 2 (a). To achieve this, the acid concentration in the resist, plotted as a function of dose, is must be a parabolic curve as shown in Fig. 2 (b). This sort of response should be compared to the classic first-order kinetic growth of acid concentration in conventional photoresists as shown in Fig. 2 (c).

In the parabolic response, the acid concentration is low at both low and high exposure doses, while the concentration reaches a maximum in the intermediate dose region. If this maximum exceeds the resist dissolution response threshold, development will produce two spaces for each space on the mask, resulting in a pitch division in the developed resist in a manner analogous to that shown in Fig. 1.

This approach to pitch division requires only a single exposure and a single development and it is fully compatible with the current manufacturing tools. The only modification required to implement the technique is a change in the resist formulation. Those advantages should make this approach cost effective.

In conventional photoresists, the production of acid as a function of dose follows the classical first order kinetic expression shown in equation (1) and plotted in Fig. 3

\[
[\text{Acid}] = [PAG]_0 (1 - e^{-k_a \times \text{Dose}}) 
\] (1)

In order to generate an acid production curve that has a parabolic like shape of the sort shown in Fig. 2 (b), there must be some way to selectively quench the acid in the high dose exposure regions.

A photobase generator (PBG) introduced into the resist will release base upon UV exposure and can be employed to accomplish the selective acid quenching. The generation of base is also a first-order kinetic process described by equation...
The simultaneous generation of acid and base is shown in Fig. 3 for a particular condition in which the initial PBG loading is higher than that of the PAG and the rate constant for base generation, $k_b$, is lower than that for acid generation, $k_a$.

Assuming the photogenerated base forms a stable salt upon reaction with the acid, the resist matrix would contain net acid or net base and a salt. The net acid concentration can be calculated simply by subtracting the base concentration from the acid concentration at each exposure dose, which yields an area of net acid production as shown in Fig. 3. This area can be plotted as a function of dose to generate a net acid production curve as shown in Fig. 4. This curve is parabola like and, in principle, capable of producing pitch division.

In order to determine the potential for pitch division, it is necessary to understand how the net acid concentration profile depends on the aerial image, the resist formulation and the kinetics of acid and base production.

![Aerial image * Exposure time](image)

Fig. 5 An acid profile with a divided pitch based on a parabolic net acid production.

The acid profile shown in Fig. 5 (b) can be constructed from the net acid curve covered by a dose range that is achieved by the given aerial image and a proper exposure time as shown in Fig. 5 (a). $H_{min}$ and $H_{max}$ are the acid concentrations in the lowest and the highest dose regions. The contrast of the acid profile is defined in equation 3.

$$\text{Contrast} = \frac{H_{max} - H_{min}}{H_{max} + H_{min}}$$

This contrast is a function of the feed ratio ([PBG]$_0$/[PAG]$_0$), the ratio of the rate constants ($k_b/k_a$) and the aerial image. For a given aerial image (generated in PROLITH 9.0), a simulation was carried out that generates a surface plot, which describes the influence of these two ratios on the contrast of the acid concentration as defined in equation 3. For a given $k_b/k_a$, the resulting plot can be used as a guide to determine the formulation (i.e. feed ratio) with the best contrast. This analysis is discussed further in the results section.

In order to explore a system of the sort described above, a test resist formulation was created based on a generic 193 nm resist co-polymer that was generously donated by DuPont.. Trisphensulphonium trifluoromethanesulfonate (TPS-Tf) was chosen as the PAG. Extensive studies have been done on PBGs [14, 15], but an o-nitrobenzylcarbamate was chosen for the initial test. The PBG was synthesized according to a published procedure [16]. The mechanism of the photolysis that produces base in this class of compounds is well characterized [17]. The structure of the PBG that was synthesized is shown in Fig. 6.
The kinetics of both acid and base generation must be considered in attempts to produce a parabola like net acid production curve. Therefore, the photolysis of both the PAG and the PBG was studied to establish these kinetic constants. The rate of acid generation from TPS-Tf was characterized by a “standard addition” method [18] in which resist formulations with varying amounts of added base quencher were tested for dose-to-clear (E0) values. The base quencher causes the E0 to shift, to higher values, which indicates higher exposure doses required to generate the net amount of acid required for threshold response. Calculation of the rate constant is discussed in the results section.

Base generation was characterized by dose-resolved quantitative infrared spectroscopy studies on the DIPA-PBG. In resist films, the o-nitrobenzyl carbamate undergoes an intramolecular disproportionation upon UV irradiation, resulting in production of o-nitrosobenzaldehyde with concomitant release of a secondary amine as shown in Fig. 7.

The nitro group has a distinct absorbance at 1525 cm⁻¹ in the infrared. Upon irradiation, the nitro absorbance peak decreases due to the conversion of the nitro group into a nitroso group, a change that can be detected by FTIR. Assuming that the rate of disappearance of the nitro group is the same as the rate of base production, the base generation can be expressed as the disappearance of the nitro functional group as a function of dose. The calculation of the rate constant is discussed in the results section.

The experimentally obtained rate constants were used to guide the resist formulation through use of the contrast plot shown in the results section. The formulation was prepared accordingly and tested in a conventional manner.

3. Experimental Section

3.1 Materials

The starting materials were all purchased from Aldrich and used without further purification. NaH (60% in mineral oil, 195 mg, 4.89 mmol) was suspended in 6 mL of dry THF. The suspension was cooled to 0 °C and stirred for 10 min. A solution of o-nitrobenzyl alcohol (624 mg, 4.07 mmol) in dry THF (2 mL) was added dropwise. The resulting mixture was stirred for 15 min after which bubbling ceased. A solution of N,N-diisopropyl carbamoyl chloride (800 mg, 4.89 mmol) in 3 mL of dry THF was then added slowly. The reaction mixture was then warmed to room temperature and stirred for 2 days. After the reaction was done, the resulting mixture was poured into a cooled mixture of H₂O (10 mL) and 2 M HCl (1.5 mL) at 0 °C and extracted with TBME (20 mL) three times. The combined organic solution was washed with saturated NaHCO₃ and brine and dried over MgSO₄. The solvent was evaporated in a rotary evaporator. Column chromatography was performed on the residue using EtOAc/Hex (1:3) to give 0.455 g of the product as a white solid. Yield: 40%, mp: 55.5 °C. IR (KBr, cm⁻¹): 1695 (s, C=O str), 1529 (s, asymmetric N-O str), 1336 (s, symmetric N-O str). ¹H-NMR (300 MHz, CDCl₃, δ): 8.05 (dd, J = 8 Hz, 4J = 1 Hz, 1H), 7.65-7.51 (m, 2H), 7.47-7.40 (dt, J = 8 Hz, 4J = 1 Hz, 1H), 5.51 (s, 2H), 4.04-3.78 (br m, 2H), 1.21 (d, J = 6.8 Hz, 12H), 13C-NMR (75.47 MHz, CDCl₃, δ): 155.08, 148.00, 134.03, 133.97, 129.40, 128.77, 125.30, 63.60, 46.47, 21.34. UV: ε₁93 = 14406, ε₂54 = 4714.

3.2 Measurement of rate constants

3.2.1 Rate constant for acid generation

A resist formulation was prepared in the following manner. DuPont polymer (5 wt %) was dissolved in propylene glycol monomethyl ether acetate (PGMEA). TPS-Tf, 10 wt % (relative to polymer) was added to the solution followed by the addition of various amounts of dicyclohexylamine (10 mol % and 13 mol % with respect to the PAG). The sample solutions were spin coated on standard silicon wafers that were pre-treated with adhesion promoter and baked at
90 °C for 1 min. The resist films were exposed stepwise to KrF laser radiation with doses increasing by an interval of 0.13 mJ/cm² per step. The post exposure bake (PEB) was performed at 90 °C for 1 min. The processed films were developed in a 2.38 % aqueous TMAH solution to provide the relief image arrays the thickness of which was measured on a J. A. Woollam M2000-V Ellipsometry. Contrast curves were constructed to quantify the influence of the base quencher loadings on the photosensitivity of the resist, from which the rate constant could be calculated.

3.2.2 Rate constant for base generation

Poly(methyl methacrylate) (PMMA) (18.6 wt %) was dissolved in diglyme and 16.7 wt % (with respect to polymer) of o-Nitro-benzyl-N,N-Diisopropycarbamate was added. The resulting solution was spin coated on a sodium chloride disk and a quartz plate at a spin speed of 1500 rpm and then baked at 100 °C for 15 min. The films were then stored under high vacuum for 3 hr to remove any residual solvent. Film thicknesses were measured on a Veeco Dektak 150 profilometer. Infrared spectra of the films were measured on a Nicolet Magna-IR 550 infrared spectrometer equipped with OMNIC software for quantitative analysis.

The films were exposed under a CYMER ELS 5400 KrF laser equipped with a light guide and a set of diverging lenses that create a relative large area of illumination with an acceptable uniformity (< 4 %).

3.3 Measurement of photosensitivity

The formulation was prepared according to the simulation results that are discussed in the results section. The DuPont 193 nm resist polymer (5 wt %), was dissolved in 2-heptanone. 4.5 wt % of TPS-Tf and 9.9 wt % of DIPA-PBG (with respect to the polymer) were then added. The solution was spin coated on silicon wafers that were previously treated with an AP 410 adhesion promoter. The resulting films were baked at 90 °C for 60 sec to produce film thicknesses of ca. 110 nm. The sample films were exposed stepwise under 248 nm UV light and then baked at 110 °C for 60 sec. After development in 2.38 % TMAH for 60 sec, the relief images were measured by ellipsometry to generate a thickness against dose plot that was used to evaluate the photosensitivity and the dual-tone response property. These experiments were also performed with 193 nm exposure.

4. Results and Discussion

4.1 Measurement of rate constants

4.1.1 Rate constant for acid generation

Fig. 8 shows the change in E₀ of the resist with varying loading of the base quencher. For high PAG loading (10 wt % to polymer), the shift in E₀ was essentially in direct proportion to the ratio of the base quencher (dicyclohexylamine) to the PAG (TPS-Tf). Thus, a linear regression was performed, generating a slope that is the reciprocal of the rate constant.

![Fig. 8 The change in E₀ of the resist as a function of base quencher loading.](image)

Fig. 8 The change in E₀ of the resist as a function of base quencher loading.

However, the rate constant obtained from that slope needs to adjusted to account for the finite absorption of the resist film, which causes the dose received at the bottom of the resist layer to be different from the incident dose. There is no change in the absorbance of the film during the exposure so the dose in any volume element can be derived from Beer’s Law, as shown below.

\[
\log \frac{I(z)}{I(0)} = a \cdot z \Rightarrow \log \frac{E(z)}{E(0)} = a \cdot z \quad (4)
\]

\[
E(z) = E(0) \cdot e^{-a \cdot z} \quad (5)
\]

Where z in equation 4 is the relative depth in the resist and a is the total absorbance of the film. In equation 5, E(z) is the true dose at the depth of z. The acid concentration through the entire resist layer is the integral of the acid concentration in each thin sublayer of the resist film.
\[ [\text{Acid}] = [\text{PAG}]_0 \cdot \int (1 - e^{-k_e x}) \, dz \quad (6) \]

\[ [\text{Acid}] = [\text{PAG}]_0 \cdot \int (1 - e^{-k_a E(0) e^{-E}}) \, dz \quad (7) \]

When the applied doses are small, first order kinetics can be assumed and accordingly, the classic approximation of \((1 - e^{-x} \approx x, x \to 0)\) can be applied.

\[ [\text{Acid}] = [\text{PAG}]_0 \cdot \int (k_a \cdot E(0) \cdot e^{-a \cdot z}) \, dz \quad (8) \]

This gives the following solution after integration:

\[ [\text{Acid}] = [\text{PAG}]_0 \cdot k_a \cdot E(0) \cdot \frac{(1 - e^{-a})}{a} \quad (9) \]

\[ k_a = \frac{[\text{Acid}]}{[\text{PAG}]_0} \cdot \frac{a}{E(0)} \cdot \frac{1}{(1 - e^{-a})} \quad (10) \]

The film that was tested is 119 nm thick and the absorbance at 248 nm is 0.066. Hence, the acid generation rate constant for TPS-Tf, according to equation 10, is 0.0575 cm\(^2\)/mJ.

4.1.2 Rate constant for base generation

Fig. 9 shows the change in the infrared spectrum of DIPA-PBG with increasing exposure dose. The decrease in the nitro absorbance peak at 1525 cm\(^{-1}\) was monitored to characterize the photolysis of the photobase generator.

The extent of conversion of DIPA-PBG was based on the disappearance of the nitro peak in comparison to a reference peak, the carbonyl absorbance of the PMMA matrix at 1730 cm\(^{-1}\). The conversion was plotted against the incident dose, as shown in Fig. 10. The first several data points in the low dose region were subjected to a linear regression.

![Fig. 10 Percent conversion against the exposure doses on the sample film](image)

Again, the rate constant is related to the slope. Unfortunately, in this case, as can be seen in Fig. 11, there are significant changes in the UV absorbance spectrum associated with the photogeneration of base.

DIPA-PBG actually undergoes photodarkening upon UV irradiation. The photodarkenig in the film complicates rate expressions considerably. However, the rate constant can still be determined numerically and was found to be 0.00243 cm\(^2\)/mJ under the experimental conditions described.

4.2 Simulation

4.2.1 Control experiments

Before any attempt is made to simulate this pitch division process, the influence of the PBG on the resist dissolution kinetics must be known. If the PAG functions as a dissolution inhibitor the simulation becomes more complex. The PBG

![Fig. 11 The UV-Vis spectra of DIPA-PBG in PMMA film upon exposure with KrF laser](image)
itself carries Lewis basic functionality prior to photolysis. It is therefore important to know whether that functionality can serve as a quencher. In order to study these issues, the non-photoactive model compound shown in Fig. 12 was synthesized. Experiments showed that the addition of this non-photoactive compound into a conventional resist formulation does not affect the $E_0$. On that basis, the simulation will assume that the addition of DIPA-PBG does not affect resist performance prior to photodecomposition.

4.2.2 Contrast considerations

The contrast of the acid profile is defined as shown in Fig. 5 and expressed in equation 3. The influence of the resist formulation ([PBG]$_0$/[PAG]$_0$) and the ratio of the rate constants ($k_b/k_a$) on the contrast is described by the plot in Fig. 13.

![Fig. 12 N,N-diisopropyl benzylearabamate, the model compound which does not undergo photolysis upon UV irradiation.](image)

![Fig. 13 A plot of contrast as a function of the formulation and rate variables. The solid line represents a formulation limit where the region below the curve meets the loading constraints. The dotted line shows the rate ratios of the experimental system that was studied.](image)

In Figure 13, the darker the region on the plot the higher the contrast. The contrast at the top right corner of the plot is zero because the moles of base generated exceed the moles of acid generated under those conditions. The dashed line on the plot marks the ratio of the rate constants for the experimental materials that were calculated from the kinetics experiments described above. It is assumed that neither the PBG nor its photoproducts serve to photosensitize the PAG.

It can be seen from Figure 13 that for fixed values of $k_a$ and $k_b$, the contrast of the net acid profile increases as the PBG fraction in the formulation increases. For this study an upper limit was set for PBG loading at 10 wt % with respect to the polymer. Hence, it is clearly an advantage to operate with the lowest PAG concentration possible.

There is also a lower limit for the absolute value of the initial PAG loading. The PAG loading defines the net amount of acid produced in the moderate dose region for fixed values of $k_a$ and $k_b$. This lower limit is the minimum amount of PAG required to produce sufficient net acid concentration to exceed the dissolution threshold.

To establish this threshold, an extrapolation of the data points in Fig. 8 was performed to find the ratio of PBG to PAG ratio at the interception of the X axis. The physical meaning of that intercept is the maximum amount of acid that can be present in the film and not clear the resist during development. That value is 0.16 mol % with respect to the initial PAG loading in the system studied. The lower limit of PAG concentration can be calculated from this value for each simulated point on the surface plot (Fig. 13).

The constraints on both PAG loading and PBG loading (< 10 wt %) were applied to the simulation and are shown in Figure 13 as a black line. The region below that line meets the loading requirement. For the particular PAG and PBG used in the test formulation, the intersection between the dashed line and the curve of the loading limit represents the optimum contrast. That process suggests a molar feed ratio of PBG to PAG of 4.2, which converted into weight ratio, gives a value of 2.85. The resist formulation was therefore prepared at 3.5 wt % of TPS-Tf and 9.9 wt % of DIPA-PBG with respect to the polymer.

The real experimental conditions, such as aerial image, spectral band width, etc., could deviate from the simulation results, but the simulation does provide guidance for the experimental work.
4.3 Dissolution modulation

Contrast curves were measured for the suggested formulation. Very weak modulation of the dissolution rate was observed. Therefore, the formulation was adjusted slightly. The PAG fraction was increased to 4.5 wt % (relative to the polymer). Contrast curves measured for the new formulation are shown in Fig. 14.

![Contrast curves for exposure at 248 nm and 193 nm for a formulation consisting of 4.5 wt % TPS-TF and 9.9 wt % DIPA-PBG with respect to the polymer.](image)

The window at 193 nm is narrower and shifted to lower exposure dose. The contrast of both the positive and negative responses is quite high, which is an encouraging observation. These experimental and simulation data suggest that this system is, in principle, capable of producing images with divided pitch.

4.4 Challenges and future work

It should be noted that the parabola like acid profile depicted in Fig. 4 is not actually a parabola. It is unsymmetrical and that asymmetry will have an impact on the fidelity of mask image transfer. Approaches to compensation for a by modification of the mask pattern and the resist formulation are being pursued. Another limitation of this approach, that is common to all of the pitch division, is that the image log slope (ILS) if the aerial image is degraded to some extent in this process. The details of the relationship between ILS, the slope of the chemical contrast curve [19] and the dissolution response function are under study. In that context, it is fortunate indeed that the dose response contrast of modern 193 nm resists is incredibly high.

Optimization of the resist formulation is now underway. PAGs with less diffusive acid will be adopted. Various PBGs are being synthesized to enable movement of the dark line in Fig. 13. The modified resist formulations will be subjected to lithographic patterning evaluation. The results of these experiments will be presented in the future.

5. Conclusions

A new pitch division approach that functions by selective acid quenching with photobase generators to create a resist profile with dual-tone response is reported. The concept was demonstrated in a series of contrast curve studies. Simulations were conducted to optimize the formulation.

Acknowledgement

The authors thank their friends and colleague, Dr. Hiroshi Ito, IBM Fellow and Hero of Chemistry for his inspiration to always combine imaging chemistry with basic science. They would also like to thank The SEMATECH Engineering Research Center for funding. SEMATECH and the SEMATECH logo are registered service marks of SEMATECH, Inc. All other service marks and trademarks are the property of their respective owners.

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