Bis Photobase Generator

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Abstract— **The extension of 193nm technology is desirable due to the magnitude of past investments. Since "optical" advancements are increasingly difficult, there is a strong demand for more sophisticated "smart" resists to increase pattern density. Many studies have proven double pattering can be used for the extension of 193nm lithography. In this study, a new class of two stage photo base generators will be introduced along with the synthetic procedure and molecular characterization. The characterizations for exposure study by NMR have shown typical characteristics to stage decomposition under the exposure of 254nm light as well as promising pitch division. GCMS was utilized to indicate the formation of photo base and major products from secondary photo chemical reaction. Kinetic simulation was also taken into account to show the consistence of proposed mechanism.**

Index Terms – **photo base generator, photo acid generator, double patterning, single exposure, pitch division, dual tone hybrid photo resist, polymer deprotection .**

I. INTRODUCTION

THE production requirement for future semiconductor that follow Moore's law has lead to many challenges in term of processing versatility and production cost. One key focus is how to extend the resolution limit of current lithographic optical tools. Processing advances have kept the next generation of lithography candidates including EUV lithography, imprint lithography or parallel e-beam direct write[1, 2] at bay. In this spirit double patterning lithography (DPL) introduced by Kawamura. Herein sub-30nm half pitch resolution was demonstrated with more processing steps and mask alignment requirements[3] than normal lithography. Later, this process was modified and simplified by Lee et al in which the double exposure was used to reduce the complication of mask alignment process[4]. Double patterning remains active research area [5-7].

Recently, the concept of pitch division has been applied to improve the resolution limits of 193nm lithography tools [8-10].Origins of the pitch division concept traces back to dual tone hybrid photo resist introduced many years ago at IBM. The composition of this new type of photoresist includes both negative tone and positive tone responses. The pitch division results from the dose distribution of the aerial image from a single exposure [11]. The figure 1, below illustrates the concept of double pattering by a single exposure.

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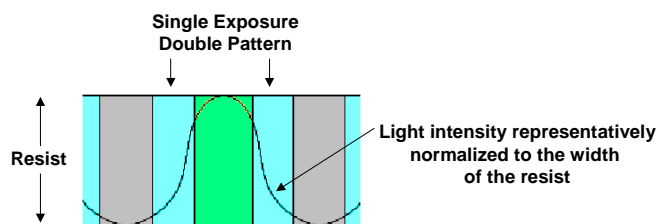
Figure 1: Double patterning by single exposure in photolithography in which grey, blue and green regions represent the acid generation insufficient to decompose polymer, acid generation sufficient to decompose polymer and base generation sufficient to reduce acid concentration such that the polymer remains intact, respectively.

Recently, Willson and coworkers introduced a new photoresist formulation for pitch division. The incorporation of both photoacid generators (PAG's) and photobase generators (PBG's) in photoresists has lead a new single exposure, double patterning lithography [12]. The mechanism of the pitch division is based on [12, 13] parabolic acid production as a function of dose, see figure 2. However, this study employed a single stage PBG whose the concentration varies linearly on the exposure doses. This affects the concentration of photo generated acid which must by higher than the response threshold concentration and thus leads to the insufficient lithographic performance, see figure 2.
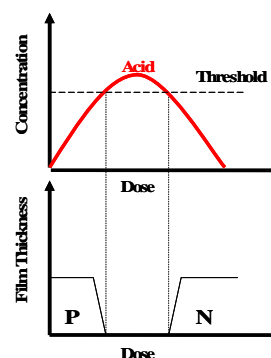

Figure 2: A parabola like acid production curve of the sort that produces a dual tone response.

In this paper, to improve the overall patterning (smaller pitch, lower linewidth roughness (LWR) etc), and the higher acid concentration for better polymer deprotection, a new class of photo base generator are introduced. The PBG breaks in two successive distinct photochemical reaction stages (figure 3) that ultimately yields a photobase for pitch division. Dosage dependence of the photobase concentration is nonlinear (figure 4) allowing for a higher acid concentration than the single stage PBG .
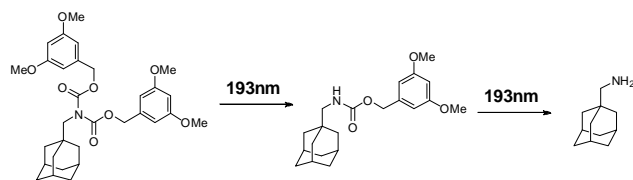
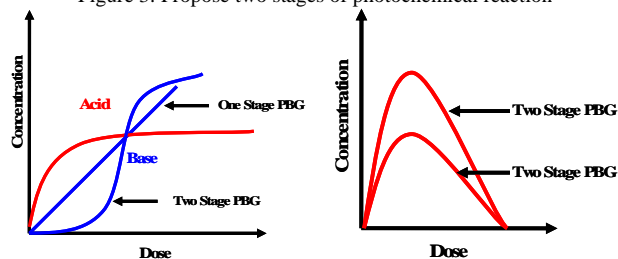Figure 3: Propose two stages of photochemical reaction

Figure 4: Comparision between concentration of base generated from one and two stage PBGs (left) and net generated acid concentration of one and two stage PBGs (right)

II. EXPERIMENTAL METHODS

Materials: The following chemicals were used without further purification: Tetramethyl Silane (TMS 99.0%) (Sigma Aldrich); Acetonitrile-d3 (ACN-d3 "100%, 99.96 atom % D) (Sigma Aldrich). Norell natural quartz 5mm NMR tube (limit 600MHz frequency, L7 in) (Sigma Aldrich)

NMR and GCMS characterization: An GCMS (model MSD Agilent Technology) and NMR (model…) were used for the characterizations. UV lamp (model …) was used for the solution exposure.

Exposure study: 1mM concentration of DMBA and DMCbzA solutions were made by Acetonitrile-d3 as a solvent. 1ml of each solution was placed in NMR quartz tubes and exposed periodically under 254nm wavelength of UV lamp along with NMR characterizations.

III. RESULTS AND DISCUSSION

Propose two stage activation of this PBG was characterized and normalized by TMS as an internal standard for the analysis. The exposures from at 0 minute (un-exposed solution) to 120 minutes focused on three peaks which have chemical shift at 3.52ppm, 2.82ppm and 2.3ppm corresponding to the signals of pro-PBG (DMBA), PBG (DMCbzA) and final base (Adamantyl methyl amine), respectively. The characteristics of these peaks and thus concentration of these species qualitatively followed characteristics of a consecutive reaction. The concentration of pro-PBG kept decreasing while final base concentration

kept increasing along with exposure times (doses). PBG is considered to be an intermediate in this photoreaction has the concentration increased at short exposure time (small doses) and decreased at long exposure times (high doses).
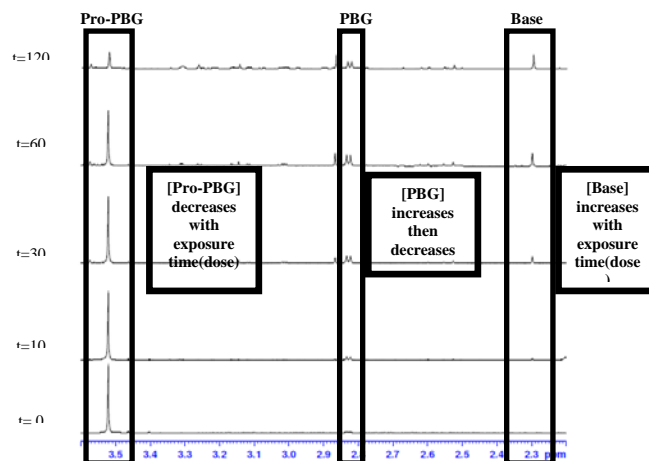
Photochemical characterizations of DMBA were based on NMR peak integration and spectra observation. Figure 4 below show the decomposition kinetic rate of 1mM solution under 254nm wavelength exposure. The reaction kinetic rate of pro-PBG was observed to follow traditional exponential decay $[Pro\text{-}PBG]_t = [Pro\text{-}PBG]_0 * e^{-It}$ where I is the dose of exposure. The characteristic of intermediate PBG (DMCbzA) and final base product which was activated from pro-PBG and PBG respectively were also observed from the spectrum. Quantitative measurements from NMR peak integration analysis have shown that almost 90% of starting material DMBA corresponding to 1mM solution was gone after 120 minutes of exposure and approximately 15% of final base was generated. This generation accounted for the conversion of DMBA to only base excluding the concentration of intermediate, DMCbzA. In addition, the conversion to final base showed the high yield at short exposure time (small doses) and gradually became steady when doses were increased. This lower quantum yield can be explained bas on the absorption of other products and bi-products which were generated during photo chemical reactions.

Compounds / Observations	3,5 Dimethoxy Benzyldehyde	Aldamantane Methylamine	Imine
GC Peak Retention Time	9.8	10.3	20.4
NMR Peak Chemical Shift	9.8	2.25	8.5

The signals of 3,5 dimethoxy Benzyldehyde, Aldamantane Methylamine and Imine formation from the exposed DMBA solutions were determined and indicated by GCMS and NMR. In order to see these components, the exposed solution must be run right after the exposure and in

specific conditions to prevent the total decomposition of Imine or complete amine reaction with benzyldehyde to form Imine. The analysis of mass spectroscopy followed GC reported the molecular masses of these above components at the retention times 9.8, 10.3 and 20.4 corresponding to 3,5 dimethoxy Benzyldehyde, Aldamantane Methylamine and Imine, respectively. These indications compromise to their signals in NMR data. The calculations for these components were based on peak integrations with chemical shifts at 9.8ppm (aldehyde), 2.25ppm (Amine) and 8.5ppm (Imine).

Ratio Exposure	$\dfrac{[Amine]+[Imine]}{[Aldehyde]+[Imine]}$	$\dfrac{[Amine]}{[Imine]}$
15 minutes	0.58	1
30 minutes	0.57	0.8
60 minutes	0.56	0.44
120 minutes	0.60	0.58

The total concentrations of Amine with Imine and Aldehyde with Imine represent the total concentrations of photo base and Aldehyde after the exposures. The ratio between the concentration of 3,5 dimethoxy benzyldehyde and photo base aldamantane methyl amine is a constant at different exposure times. This is well matched the stoichiometry of the reaction 1 of DMBA photo chemical reaction which produces aldehyde and amine with the mole ratio 2:1. Besides, the mole ratio of amine and Imine was also taken into account at different exposures. Data show this ratio decreases along with longer exposure times, this could be explained by the formation of Imine in which concentration of Amine decreases and concentration of Imine increase over time. However, according to reaction 3, the decomposition of Imine led to the increase of both above ratios at very long exposure times.
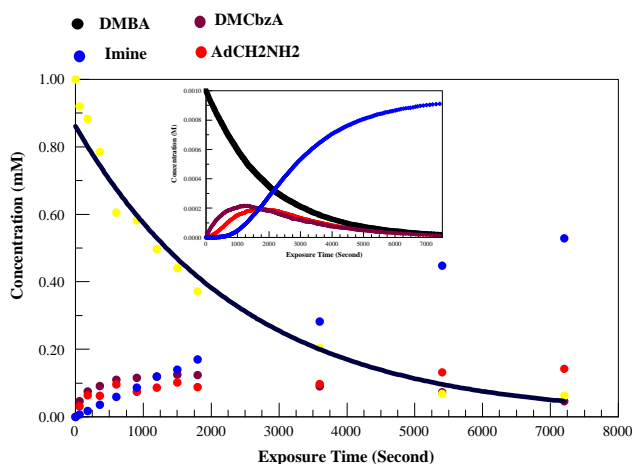

The kinetic simulation was done by using "Chemical Kinetic Simulator" software provided by IBM. The mechanism was followed the above proposed mechanism where trial kinetic rate constant for reaction (1), (2), (3), (4) an (5) were k_1 = k_2 k_3 k_4 k_5 , respectively. Results from the simulation showed that the simulated data and experimental data are well-matched and consistent. The concentration of DMBA is

exponentially decayed while DMCbzA, Amine an Imine plays a role as intermediates in steady state reactions. There for their concentration increase at the beginning with small doses and decrease along with higher doses. The slightly mismatched between the theoretical data (simulation) and experimental data is the concentration of Amine at very long exposure times where concentration has a tendency to get steady and constant. This could be explained by the reverse decomposition from Imine back to amine. This generated concentration added and compensated to the loss of amine reacted to 3,5 dimethoxy benzyldehyde for the formation of Imine. Besides, the kinetic characteristics of generated photo base were also shown by the kinetic simulation. The expanded graph at low exposure doses indicated the non linear behavior of base concentration as a function of dose. This compromises to the expected characteristics of two stage photo base generator.
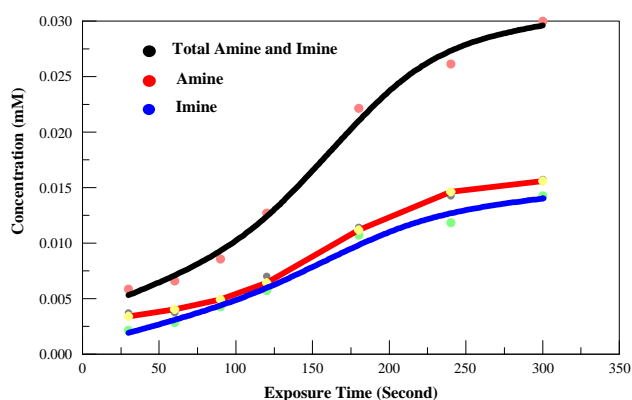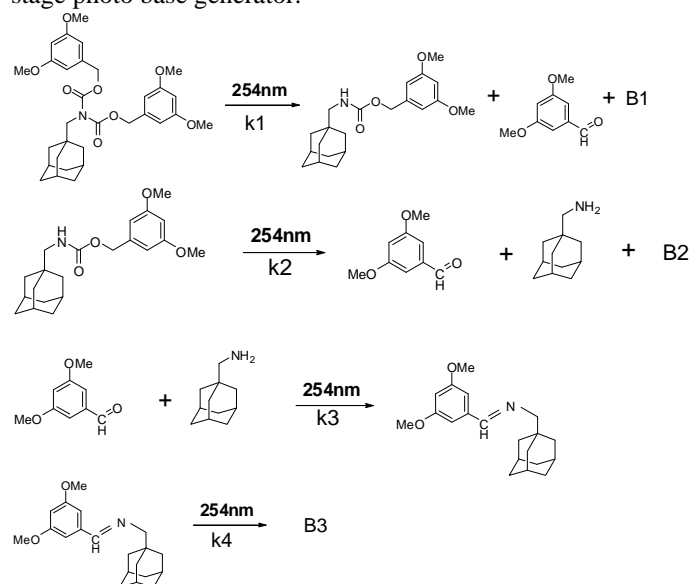

The experimental data from exposed DMBA solution strongly focused on very low exposure doses or very short exposure times. In the first 5 minutes of exposure, the yield of converted DMBA to major products including aldehyde and amine is almost 100 percent. The total concentration of amine and Imine from the Schiff base formation reflects the true amount of base that could be used to quench acid generated from photo acid generator for further lithographic

studies. Consistently, this total concentration when graphed as a function of dose indicated a non linear curve characteristic. This behavior of amine at low exposure doses or short exposure times was expected and followed the kinetic simulation shown above.
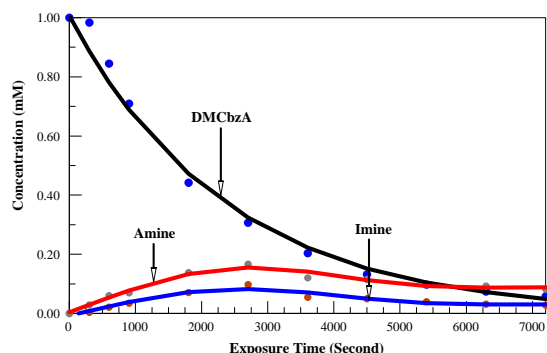
One of the major intermediates was taken into account for photo chemical reaction and kinetic study. DMCbzA is considered one stage photo base generator which is also can be used to generate photo base Adamantane methylamine. The exposure study was carried out with the same manners as two stage photo base generator DMBA. The plots of starting material DMCbzA, photo generated amine and Imine formation as a function of doses were shown in figure 9. With the same characteristic, DMCbzA undergoes photo chemical reaction and shows exponential decay. Amine and Imine also indicate the characteristics of intermediates in a steady state reaction in which the concentrations increase at the beginning and fall back along with higher doses. The overall photo chemical reactions in exposed DMCbzA reaction can be proposed below with the characteristics matching experimental kinetic data. However, due to different structures an thus mechanism, the concentration of photo products including amine and Imine are slightly different from exposed DMBA solution.
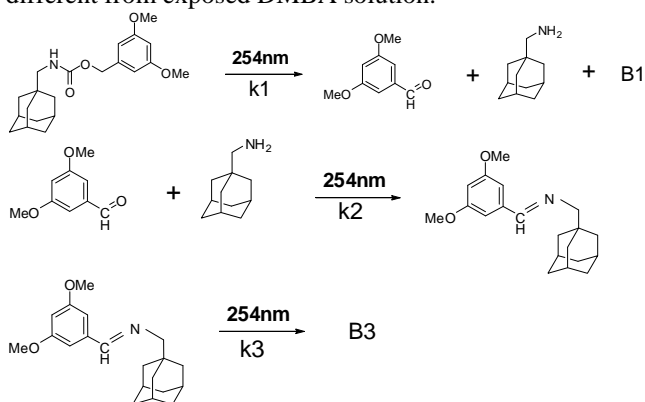
CONCLUSIONS

minutes by evaporation-induced method. This very short deposition time would great for industrial applications.

REFERENCE

[1] B. J. Lin, *Microelectronic Engineering 83*, 604-613.

[2] R. H. French and H. V. Tran, *Annual Review of Materials Research* **2009**, *39*, 93-126.

[3] D. Kawamura, K. Kaneyama, S. Kobayashi, J. J. S. Santillan and T. Itani, *Advances in Resist Materials and Processing Technology XXV* (San Jose, CA, USA) **2008**, pp. 692313-692310.

[4] S. Lee, K. Jen, C. G. Willson, J. Byers, P. Zimmerman and N. J. Turro, *Journal of Micro/Nanolithography, MEMS and MOEMS* **2009**, *8*, 011011-011011.

[5] U. Iessi, S. Loi, A. Salerno, P. Rigolli, E. De Chiara, C. Turco, R. Colombo, M. Polli and A. Mani, *Optical Microlithography XXI* (San Jose, CA, USA) **2008**, pp. 692428-692410.

[6] J. Finders, M. Dusa, B. Vleeming, H. Megens, B. Hepp, M. Maenhoudt, S. Cheng and T. Vandeweyer, *Optical Microlithography XXI* (San Jose, CA, USA) **2008**, pp. 692408-692412.

[7] S. Tarutani, H. Tsubaki and S. Kanna, *Advances in Resist Materials and Processing Technology XXV* (San Jose, CA, USA) **2008**, pp. 69230F-69238.

[8] C. Bencher, Y. Chen, H. Dai, W. Montgomery and L. Huli, *Optical Microlithography XXI* (San Jose, CA, USA) **2008**, pp. 69244E-69247.

[9] C. Fonseca, M. Somervell, S. Scheer, W. Printz, K. Nafus, S. Hatakeyama, Y. Kuwahara, T. Niwa, S. Bernard and R. Gronheid, *Optical Microlithography XXII* (San Jose, CA, USA) **2009**, pp. 72740I-72712.

[10] W. Shiu, H. J. Liu, J. S. Wu, T.-L. Tseng, C. T. Liao, C. M. Liao, J. Liu and T. Wang, *Optical Microlithography XXII* (San Jose, CA, USA) **2009**, pp. 72740E-72747.

[11] M.C. Hakey, D.V. Horak, A.D. Katnani, N.M. Patel, and P.A. Rabidouxy in *Frequency doubling hybrid photoresist having negative and positive tone components and method of preparing the same*, *Vol.* US, **2000**.

[12] X. Gu, C. M. Bates, Y. Cho, T. Kawakami, T. Nagai, T. Ogata, A. K. Sundaresan, N. J. Turro, R. Bristol, P. Zimmerman and C. G. Willson, *Advances in Resist Materials and Processing Technology XXVII* (San Jose, California, USA) pp. 763906-763912.

[13] X. Gu, C. Bates, Y. Cho, E. Costner, F. Marzuka, T. Nagai, T. Ogata, C. Shi, A. K. Sundaresan, N. J. Turro, R. Bristol, P. Zimmerman and C. G. Wilson, *Journal of Photopolymer Science and Technology* **2009**, *22*, 773-781.