

# Combinatorial methodologies offer potential for rapid research of photoresist materials and formulations

Joseph L. Lenhart,<sup>a)</sup> Ronald L. Jones, Eric K. Lin, Christopher L. Soles, and Wen-li Wu  
National Institute of Standards and Technology, 100 Bureau Drive, Stop 8541, Gaithersburg,  
Maryland 20899-8541

Dario L. Goldfarb and Marie Angelopoulos  
IBM T. J. Watson Research Center, Yorktown Heights, New York 10598

(Received 1 June 2001; accepted 28 January 2002)

A combinatorial research methodology is outlined with the potential to investigate material factors in photoresist formulations *more rapidly* than with traditional experimental design. The approach involves generating a gradient of processing variables in the photoresist film and using a set of analysis tools to “map” the photoresist properties as a function of the gradient variables. While high-throughput strategies have proven useful for empirical optimization of photoresist processing conditions, they have not been fully exploited to probe the complex array of material issues in projection lithography. Of primary importance in combinatorial methodologies is the generation of variable gradients. The focus of this article is to illustrate techniques to generate a gradient in bake temperature and bake time in the polymer films, and to illustrate that these gradient techniques can be used to probe fundamental properties of lithographic materials, such as deprotection kinetics. These gradient techniques were applied to rapidly probe the deprotection behavior of a poly(tertbutyloxy-carbonyloxy-styrene). The deprotection data, obtained by applying the combinatorial gradients, agrees well with previous literature, validating the accuracy of these high throughput methods. The advantage of the combinatorial research strategies lies in the potential to investigate fundamental lithographic phenomena more rapidly than with traditional experimentation. © 2002 American Vacuum Society. [DOI: 10.1116/1.1463069]

## I. INTRODUCTION

The fabrication of sub-100 nm features via photolithography requires fine control of the critical dimension (CD), shape, and line-edge roughness (LER). Many photoresist material factors can impact both CD and LER, including segregation of the photoacid generator molecules or resist additives,<sup>1</sup> photogenerated acid diffusion,<sup>2</sup> outgassing of photoresist materials,<sup>3</sup> film thickness effects,<sup>4</sup> and copolymer composition and phase separation between protected and deprotected polymers at the interface between exposed and unexposed areas.<sup>5</sup> In addition, several process variables require optimization such as exposure dose, postexposure bake times and temperatures, and developing time,<sup>6</sup> and it is not completely understood how these factors contribute to LER and CD. Due to this complexity, development and optimization of resist systems or formulations is time consuming. Integration of combinatorial techniques with traditional research and development provides a powerful approach to *rapidly* conduct lithographic materials research. In this work a combinatorial research and development method is outlined with the focus of developing gradients of bake temperature and time in polymer films. These gradients are used to probe the composition driven catalysis of the deprotection of poly(tertbutyloxy-carbonyloxy-styrene) (PBOCSt) by hy-

droxyl moieties on polyhydroxystyrene (PHS). The gradients were also used to study the acid catalyzed deprotection of a model PBOCSt/photoacid generator system.

Combinatorial methods entail simultaneously varying system variables over a wide range of values for rapid prototyping. Combinatorial protein and drug screening methods are common techniques in the pharmaceutical and biotechnology industries.<sup>7,8</sup> Combinatorial techniques have recently been adapted to probe fundamental polymer science issues such as the phase behavior of polymer blends,<sup>9</sup> and polymer thin-film dewetting.<sup>10</sup> By applying similar methodologies to photolithography, crucial materials issues can be identified in a rapid manner. Combinatorial techniques are already the basis of the standard dose-focus matrix, and have been applied in a limited fashion in photoresist materials research.<sup>11</sup> Here we illustrate several additional areas in the field of lithography where combinatorial methods can prove to be highly beneficial. It is important to note that a requirement of combinatorial methodologies is that they provide identical information to traditional experimental design strategies. The true advantage of combinatorial approaches lies in the ability to generate data *more rapidly* than with traditional methods, leading to higher productivity and quicker product research and development cycles. The rapidity of the data generation can be achieved by overcoming the mindset of traditional experimentation, where a single sample is exposed to one set of experimental conditions. With combinatorial techniques a single sample is exposed to a wide range of experimental conditions, allowing for more rapid research on a smaller sample set.

<sup>a)</sup>Author to whom correspondence should be addressed; electronic mail: joseph.lenhart@nist.gov

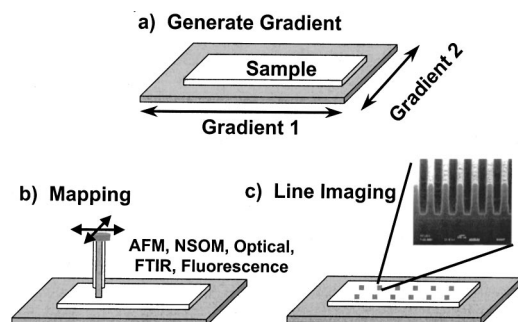


FIG. 1. Schematic of the combinatorial methodology.

## II. COMBINATORIAL APPROACH

The purpose of this article is to outline a combinatorial methodology that can be applied to rapidly conduct photoresist material research. The combinatorial approach involves three steps: (1) generating a gradient in an appropriate materials variable, (2) mapping the properties of the photoresist, and (3) developing line structures in different regions of the film. The entire methodology is briefly outlined in this article, with the first aspect (step 1) being examined in detail, setting the basis for future investigations extended to the overall combinatorial approach. A schematic of the combinatorial methodology for photoresist materials research is shown in Fig. 1. The first step [Fig. 1(a)] is to generate the appropriate gradient in the photoresist film. The types of gradients that can currently be imposed are film thickness,<sup>10</sup> polymer blend composition,<sup>9</sup> and temperature.<sup>9,10</sup> This report focuses on imposing temperature and time gradients in polymer films. In principle it is possible to simultaneously impose two orthogonal gradients in the polymer film to study both variables. Orthogonal gradients in temperature and composition were recently used to rapidly develop the phase diagram of a polymer blend.<sup>9</sup>

The second step in the combinatorial approach is to evaluate the photoresist properties as a function of the gradient variables [Fig. 1(b)]. This involves “mapping” the properties of the photoresist film at different positions with an analysis tool of appropriate resolution. The spatial resolution of the tool should be significantly smaller than the distance of the imposed variable gradient [Fig. 1(a)]. Some useful tools with nanometer scale resolution are atomic force microscopy and near field optical microscopy. Additional tools such as fluorescence, infrared, and optical microscopy can provide micron resolution. Even tools such as secondary ion mass spectroscopy, x-ray photoelectron spectroscopy, and ellipsometry (each with millimeter scale spatial resolution) are useful if the variable gradient is imposed over a distance of several centimeters. A general requirement for these “mapping” tools is that the technique resolution must be small enough that significant changes in the photoresist properties do not occur over this distance due to the imposed gradient.

In principle, patterns can be generated at different positions on the film [Fig. 1(c), a technique already in use by the industry]. Scanning electron microscopy (SEM) can be used to evaluate the pattern quality [Fig. 1(c)] as a function of the

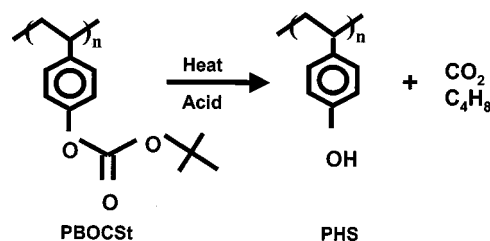


FIG. 2. Deprotection reaction of PBOCSt (left) to PHS (right).

photoresist film properties [Fig. 1(b)] and the gradient variables [Fig. 1(a)].

## III. EXPERIMENT

Unless otherwise stated, all chemicals were used as obtained from Aldrich Chemical Company (Milwaukee, WI). A model polymer system composed of a blend of a fully protected polymer PBOCSt and a fully deprotected polymer PHS was employed (see Fig. 2). Varying ratios of PBOCSt and PHS were dissolved in propylene glycol methyl ether acetate (PGMEA) and spin cast onto clean silicon wafers at  $(1500 \pm 10)$  rpm for  $(90 \pm 5)$  s. The total mass fraction of polymer in the PGMEA was kept constant at  $(5 \pm 0.05)\%$  to maintain a constant thickness for each of the blend compositions. After spin coating, the films were placed under vacuum at room temperature for  $(2 \pm 0.2)$  h to remove residual PGMEA. However, the amount of residual PGMEA in the blend films was not quantified. Fourier transform infrared spectroscopy (FTIR) was conducted on the polymer layers with a Nicolet Magna 550 FTIR (Madison, WI) using 1600 scans at a resolution of  $4 \text{ cm}^{-1}$  and a mercury–cadmium–telluride detector.<sup>12</sup>

## IV. RESULTS AND DISCUSSION

The deprotection reaction converting the protected polymer (PBOCSt) to the deprotected polymer (PHS) is shown in Fig. 2. While a photogenerated acid usually catalyzes this reaction, deprotection can be thermally induced. In addition, the PHS hydroxyl moieties are acidic and can also catalyze this reaction,<sup>13–15</sup> leading to thermal induced deprotection (degradation) at lower temperatures and faster rates with increasing PHS monomer concentration. Wallraff *et al.* observed a slow induction period for PBOCSt thermolysis, followed by rapid reaction consistent with the autocatalytic behavior expected from PHS catalyzed deprotection.<sup>14</sup> Ito observed that this hydroxyl-catalyzed deprotection could only occur in systems where the PHS is in intimate contact with the PBOCSt groups.<sup>15</sup> So phase separation or blocky copolymer composition could reduce the autocatalytic effect of PHS.

Here, a combinatorial approach was taken to rapidly map the thermal deprotection (degradation) temperature of PBOCSt as a function of the PHS content in a blend film of PBOCSt/PHS. While true photoresists are copolymers rather than a blend, and contain a photoactive acid generator (PAG) as well as other additives, this combinatorial gradient-

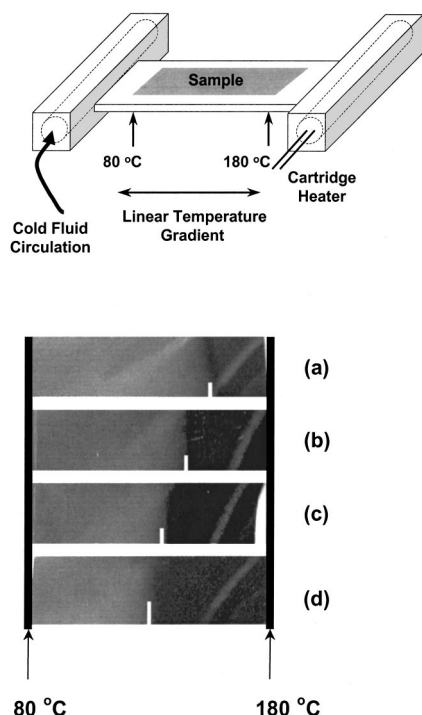


FIG. 3. (Top) Schematic of the combinatorial temperature gradient apparatus. (Bottom) Optical micrographs of PBOCSt/PHS blend films after annealing on a temperature gradient. Shown are blend compositions of: (a) 90 wt %, (b) 80 wt %, (c) 70 wt %, and (d) 60 wt % PBOCSt. The temperature gradient is linear and lengthwise, with the dark lines signifying the extremes of 80 °C (left) and 180 °C (right). White line indicators show crossover positions used to estimate temperatures in Fig. 4.

based approach is general and would easily provide similar information on industrially relevant photoresists. Given that one primary purpose of this article is to illustrate that the combinatorial gradients provide the same information as traditional experimentation, a widely studied system of PBOCSt/PHS was chosen. In addition candidate 157 nm resists are similar to PBOCSt where some hydrogen atoms are replaced by fluorine.

Blend films with various PBOCSt/PHS mass ratios were spun onto silicon wafers and the wafers placed on an aluminum block, as shown in Fig. 3 (top). One end of the aluminum block was held at  $(180 \pm 1)^\circ\text{C}$  with a cartridge heater while the other end was held at  $(80 \pm 1)^\circ\text{C}$  using a cold fluid bath, thereby producing a linear temperature gradient from (80 to 180) °C over a 4 cm distance on the block. This equipment is described in more detail elsewhere.<sup>9,10</sup> By using thin ( $\sim 1$  mm) silicon wafer substrates, the temperature gradient can be rapidly transferred to the photoresist film. After  $(15 \pm 0.5)$  min exposure to the temperature gradient, the samples were removed and quenched to room temperature on a cold brass block. A sharp color transition occurs in all the films, with a light blue color at the low temperature side of the wafer (the same light blue color as the “as cast” film) and a dark blue at higher temperatures. The position of the color transition was dependent on the blend composition, as shown in Fig. 3 (bottom). Since the initial “as cast” blend films were uniformly light blue in color, the dark blue transition

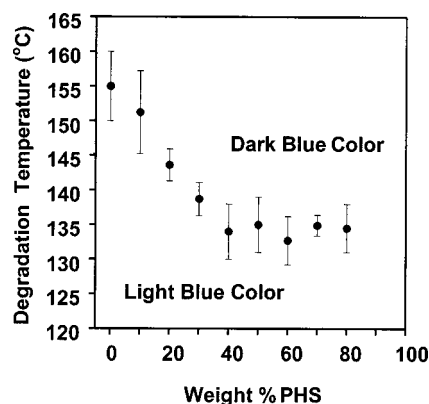


FIG. 4. Temperature of the color transition (thermal degradation temperature) in the blend films is shown as a function of blend composition. Above the curve, the samples displayed a dark blue color. Below the curve, the samples retained their initial light blue color. The data show the catalytic influence of hydroxyl moieties from PHS on the PBOCSt decomposition.

indicates a dramatic change in the film structure at elevated temperatures. The color change displays a kinetic dependence, with the films at higher temperatures going through the color transition more rapidly.

Since the temperature gradient in Fig. 3 is linear, the position of the color change can be converted into a temperature. Figure 4 plots the transition temperature as a function of the mass fraction of PHS. At temperatures above the data points, the dark blue color is observed, while at lower temperatures the film maintains its initial light blue color. The power of the combinatorial approach is that the data for Fig. 4 were generated very rapidly, with the level of uncertainty indicated by the error bars representing the standard deviation of four separate runs. This uncertainty is not particularly large as thermogravimetric analysis typically yields a 10 °C temperature spread for the mass loss from deprotection.

The color transition in Fig. 3 is caused by a decrease in film thickness, due to volatile carbon dioxide and butene during deprotection. Specular x-ray reflectivity (SXR) was used to quantify thickness changes in the blend films. Separate films were made for the SXR measurements. A 100% PBOCSt film showed a  $(37\% \pm 5\%)$  decrease in film thickness after annealing at 180 °C for 15 min. This is consistent with near complete deprotection of the PBOCSt film and the associated mass loss from volatile carbon dioxide and butene. The sample thickness was measured using SXR in the as-cast state, and then remeasured after annealing. Annealing conditions were chosen based on Fig. 4 to provide a color change in the blend film. A blend film of 50% PBOCSt/50% PHS showed a  $(20\% \pm 5\%)$  decrease in film thickness after annealing at elevated temperatures. Due to the large sample area probed by SXR, the technique was not employed on the combinatorial samples exposed to the temperature gradient. However, ellipsometry (a technique frequently used in semiconductor research) is a potential alternative with suitable resolution for “mapping” thickness changes on the combinatorial samples.

Figure 4 shows the catalytic influence of the hydroxyl groups from PHS on the thermal deprotection of PBOCSt.

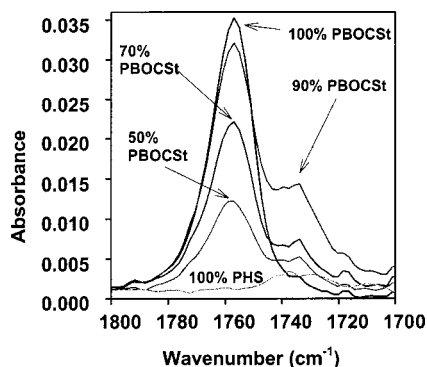


FIG. 5. FTIR scans are shown for the initial as cast blend films. The shoulder ( $1730\text{ cm}^{-1}$ ) on the larger carbonyl peak ( $1755\text{ cm}^{-1}$ ) indicates hydrogen bonding between hydroxyl groups on PHS and the carbonyl on PBOCSt. This indicates intimate mixing of the PBOCSt/PHS polymers in the as cast blend films. The bottom curve is the FTIR spectrum for a 100% PHS film, which contains no absorption in this region.

As the PHS content increases, the degradation temperature decreases. It is observed that phase separation of PBOCSt/PHS blend films would decrease the catalytic ability of PHS on the deprotection reaction.<sup>15</sup> To test for phase separation in these films, representative samples were examined using tapping mode atomic force microscopy (AFM). Phase separation in thin films often produces a morphological transition when the high surface energy phase is encapsulated by the lower surface energy phase. This produces an inhomogeneous structure parallel to the substrate, which can result in a slowly varying height modulation. Topographic scans of the as-cast films show a rms roughness ranging from (15 to 25) Å. This value is larger than roughness typically observed in pure homopolymer films, and might indicate that the “as cast” blend films have formed small phase separated domains. Scans of the high temperature region (dark blue color) reveal a significantly lower roughness relative to the low temperature regions of the film (light blue color). This reduction in surface roughness upon annealing suggests that the films do not phase separate at the elevated temperatures, but rather become more uniform, consistent with complete deprotection and the formation of a single polymer phase. It should also be noted that scans using the phase mode of the AFM revealed no significant phase shift in either region.

To further test for phase separation in the initial as cast films, Fourier transform infrared (FTIR) spectroscopy was conducted on each of the samples. PBOCSt absorbs strongly near  $1750\text{ cm}^{-1}$  due to the carbonyl stretching vibration (see Fig. 2). When the carbonyl band is hydrogen bonded to a hydroxyl group on PHS, a shoulder appears in the carbonyl absorption near  $1730\text{ cm}^{-1}$ .<sup>15</sup> Figure 5 shows FTIR spectra of the as cast PBOCSt film, as well as various blend films of PBOCSt/PHS. For 100% PBOCSt no shoulder appears on the carbonyl peak. However for the PBOCSt/PHS blend films, a clear shoulder is observed, indicating that carbonyl groups on PBOCSt are hydrogen bound to the hydroxyl groups on PHS. Since intimate mixing between PBOCSt and PHS is required for hydrogen bonding, this suggests that the thermal deprotection data in Fig. 4 are not influenced by

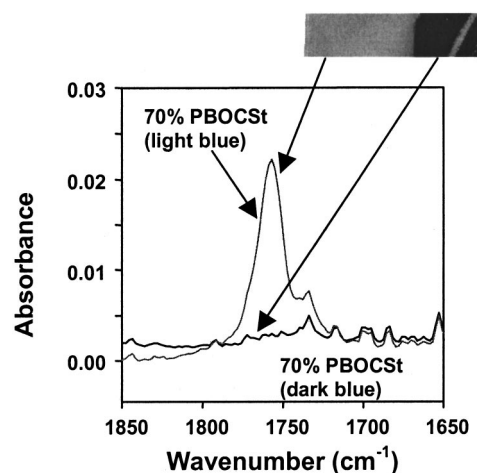


FIG. 6. FTIR scans are shown for a 70% PBOCSt/30% PHS blend film after application on the temperature gradient stage. The light blue region of the film (initial as cast color) shows strong carbonyl absorption. The dark blue region of the film showed no carbonyl absorbance indicating complete deprotection.

phase separation of the blend films. 100% PHS absorption is also shown in Fig. 5 and displays no carbonyl band.

SXR confirmed shrinkage of the film at elevated temperatures. This film shrinkage is due to the deprotection reaction and the release of carbon dioxide and butene from the film (see Fig. 2). Control experiments on pure PBOCSt and PHS films were conducted to verify that the color transition in Fig. 3 corresponds to deprotection. While the 100% PHS film did not show a color change over the entire range of the temperature gradient, the pure PBOCSt layer did show a color transition between (150 and 160) °C. FTIR verifies that the dark blue color corresponds to deprotection.

Figure 6 shows FTIR spectra for a film with a mass fraction of 70% PBOCSt/30% PHS after exposure to the temperature gradient. The strong carbonyl absorbance in the top spectrum, taken in the light blue region of the film, indicates that the PBOCSt remains protected. The bottom spectrum was taken in the dark blue region. Absence of the carbonyl stretch in the dark blue region of the film verifies the deprotection, confirming that the data points in Fig. 4 indicate a boundary of deprotection for the PBOCSt. Hydroxyl residues on the PHS catalyze the thermal deprotection of PBOCSt. It is interesting that the color change in pure PBOCSt occurs near 160 °C rather than the expected value of 190 °C,<sup>16</sup> as measured by thermogravimetric analysis (TGA). This could suggest that the PBOCSt polymer used here was partially deprotected. However, the thickness decrease is consistent with the expected mass loss of a completely protected polymer. It is likely that the difference in the thermal degradation is due to differences in the time scales of the TGA and combinatorial measurements. The combinatorial samples were exposed to the baking temperature for 15 min. These combinatorial results agree well with the work of Wallraff *et al.* who showed that PBOCSt will degrade at 150 °C in (15–30) min<sup>14</sup> due to the autocatalytic influence of the hydroxyl groups on PHS.



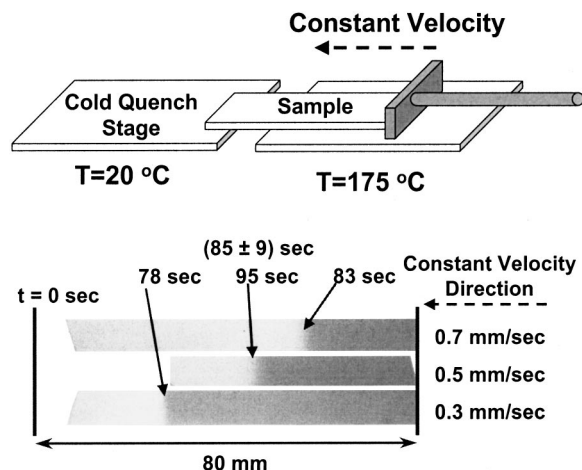


FIG. 7. (Top) Apparatus for generating a gradient in bake time in polymer films. (Bottom) Color transition in 100% PBOCSt films after being pushed across the baking stage at different velocities. The position of the color transition is easily related to the degradation time.

The influence of PHS concentration on PBOCSt deprotection slows at PHS mass fractions greater than 30%. This corresponds to a thermal degradation temperature between (130 and 138) °C. The plateau in the degradation temperature with increasing PHS fractions could be due to chain mobility effects. Since the glass transition temperature of PBOCSt is near 130 °C, hindered chain mobility could slow the PHS catalyzed deprotection at these lower temperatures as the protective group on PBOCSt would have more trouble “finding” the catalytic hydroxyl groups on PHS. Ito observed similar behavior, finding that hydroxyl induced thermolysis of PBOCSt primarily takes place at temperatures above 130 °C.<sup>15</sup>

In addition to generating a temperature gradient in the polymer film, a gradient in bake time was also developed. Figure 7 (top) shows a schematic of the apparatus. The polymer sample starts on a baking stage. The sample is pushed across the stage at a constant velocity onto a cold quenching stage that essentially freezes in the polymer properties. The left regions of the sample are exposed to the bake temperature for short periods of time, the far right region to longer bake times. 100% PBOCSt films were placed on the heating stage, held at  $175 \pm 4$  °C, and pushed across the baking stage at three different velocities. A clear color change occurs in the PBOCSt film due to the deprotection reaction. Since the initial starting point of the sample, the pushing velocity, and the total distance traveled by the sample are known, the position of the color transition can be related to a degradation time. For the three different velocities, the degradation time was  $(85 \pm 9)$  s, illustrating reproducibility of the time gradient apparatus to 10%. At this point we have not related the extent of the deprotection at this color transition. Careful inspection shows that there is actually a gradient in the film color near the color transition (a gradient in film thickness).

A PBOCSt film was loaded with 4% by weight of a PAG, bis(*p*-tert-butylphenyl) iodonium perfluorooctanesulfonate (PFOS). The PBOCSt/PFOS films were blanket exposed to ultraviolet (UV) radiation from a broad band source ranging

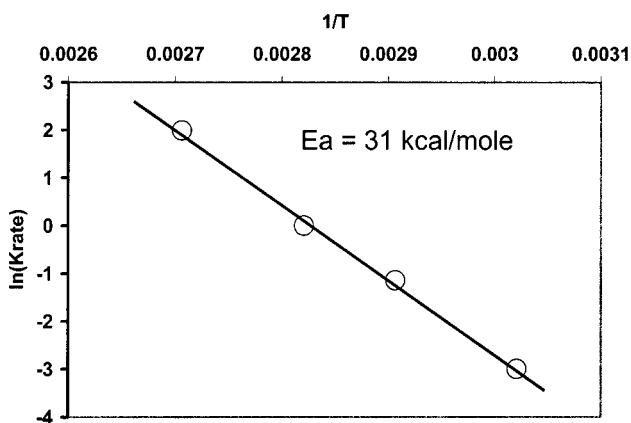
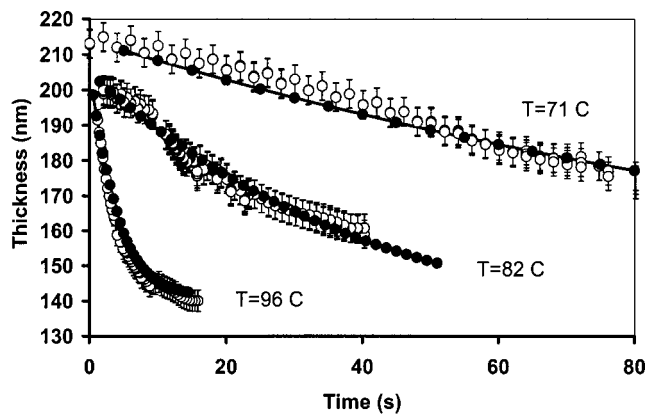
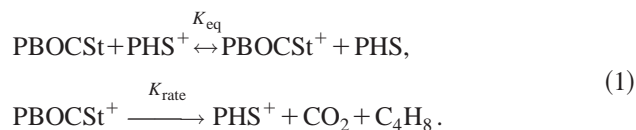


FIG. 8. (Top) Isothermal reaction kinetic data (open circles) for the deprotection of PBOCSt/PFOS films at several different temperatures (96, 82, and 71 °C). The data was obtained by pushing the samples across the baking stage onto a cold stage (see Fig. 7). The filled circles represent the fit to the data, assuming the kinetic model in Eq. (1). The error bars represent a maximum standard deviation in the thickness measurements from several samples pushed across the baking stage at different velocities. (Bottom) Arrhenius plot over a temperature range of (57–96) °C, for rate constants obtained from the kinetic fits. The activation energy for the first order reaction rate constant  $K_{\text{rate}}$  in Eq. (1) is  $(31 \pm 2)$  kcal/mole.

between (220 and 260) nm with a total dose of 500 mJ/cm<sup>2</sup>, in order to generate the acid, and placed on the baking stage (see Fig. 7). The samples were pushed across the stage at a constant velocity. A gradual color transition occurred in these samples due to the deprotection reaction of PBOCSt and the resulting film shrinkage. The thickness of the film was measured at different positions on the wafer using a Filmetrics F20 UV-visible interferometer with a 0.5 mm spot diameter and a standard uncertainty of  $\pm 1$  nm for the film thickness. Since the film position can be directly related to the time at the baking stage temperature, the reaction kinetics can be followed. These kinetic data are shown in Fig. 8. The open circles represent the film thickness at particular positions on the sample (converted to time). The filled circles represent a kinetic fit to the data using the deprotection model of Wallraff *et al.*<sup>17</sup>



This model assumes a competition between the PHS and PBOCSt monomers for the photogenerated acids. This equilibrium step occurs quickly, and the equilibrium constant  $K_{eq}$  governs the amount of acidified PBOCSt groups ( $PBOCSt^+$ ). The  $PBOCSt^+$  then decomposes with a first order reaction rate constant  $K_{rate}$ . Using an equilibrium constant of 1.3 (similar to Wallraff *et al.*<sup>17</sup>), the data could be adequately fit and the rate constant extracted. In our kinetic fit we assume the film thickness directly follows the deprotection kinetics, a reasonable assumption for PBOCSt systems.<sup>18</sup> The bottom portion of Fig. 8 shows the plot of  $\ln(K_{rate})$  versus the inverse temperature. The activation energy obtained from the linear fit was  $(31 \pm 2)$  kcal/mole, in good agreement with the literature.<sup>14,17</sup>

The potential advantage of the combinatorial temperature and time gradient techniques is that a single sample can be exposed to a range of times and temperatures, allowing for more rapid investigation than with traditional experimental design. Here we include a rough calculation to show this increase in efficiency. For Fig. 4, each composition point was gathered by applying samples on the temperature gradient stage for 15 min per sample. Since nine compositions were measured, the total measurement time for Fig. 4 was 2 h 15 min. The data in Fig. 4 have an uncertainty of  $\pm 5^\circ\text{C}$ . Placing individual samples of the same compositions in an oven at different temperatures would require 16 measurements (every  $5^\circ\text{C}$  from 100 to  $180^\circ\text{C}$ ), to generate the same graph (Fig. 4) with similar  $5^\circ\text{C}$  uncertainty over the same temperature range. Each temperature would be held for 15 min for a total of 4 h. Using the combinatorial approach takes  $\sim 1/2$  the time in this case to generate the same data.

Unlike traditional experimentation, which is limited by a single experimental condition per sample, significant potential exists with the combinatorial techniques to further improve this efficiency by imposing multiple orthogonal gradients on a single sample. For example, if the PBOCSt/PHS films contained a blend composition gradient on the sample, similar to Merideth *et al.*,<sup>9</sup> then the entire data set in Fig. 4 could be generated on a single sample in 15 min ( $\sim 1/16$  the time required for traditional experimentation). In another example, if the baking stage in Fig. 7 actually contained a temperature gradient orthogonal to the pushing velocity, then one sample could be used to generate the entire deprotection kinetic data over a range of temperatures. The current temperature gradient apparatus used in this study was too small for this. However, a larger model is currently being designed to allow orthogonal temperature and time gradients. In addition with combinatorial techniques, the data analysis time can be decreased significantly. Since the entire temperature and time range is contained on a single sample, the “mapping” tools can be automated leaving the experimenter free to conduct other research. For example, the thickness measurements in Fig. 8 were made using a programmable stage in order to “map” the extent of deprotection/thickness at different positions on the sample.

## V. CONCLUSIONS

A combinatorial methodology was outlined with the potential to explore material science issues in projection lithography more rapidly than with traditional experimental design. This methodology involves three distinct steps including: (a) gradient generation in the photoresist, (b) mapping of the photoresist material properties, and (c) dissolution and SEM imaging of the developed line features. While high throughput techniques have proven useful in process optimization, the approach can be further utilized in photoresist materials to facilitate research and development. The major advantage of the combinatorial methodology is the ability to generate data over a wide range of system variables simultaneously. This article demonstrates techniques to generate both temperature and time gradients in polymer films. Additional combinatorial techniques are being developed to impose a gradient in exposure dose/time, dissolution time, and composition of the photoresist formulation.

## ACKNOWLEDGMENTS

This work was funded in part by DARPA, Contract No. N66001-00-C-8803. J. L. L. and C. L. S. are grateful to the National Research Council for postdoctoral funding.

Presented at the 45th International Conference on Electron, Ion, and Photon Beam Technology and Nanofabrication, Washington, DC, 29 May–1 June 2001.

- <sup>1</sup>K. E. Uhrich, E. Reichmanis, and F. A. Baiocchi, *Chem. Mater.* **6**, 295 (1994).
- <sup>2</sup>T. H. Fedynyshyn, J. W. Thackeray, J. H. Georger, and M. D. Denison, *J. Vac. Sci. Technol. B* **12**, 3888 (1994).
- <sup>3</sup>P. M. Detinger, *J. Vac. Sci. Technol. A* **18**, 3364 (2000).
- <sup>4</sup>D. S. Fryer, P. F. Nealey, and J. J. de Pablo, *J. Vac. Sci. Technol. B* **18**, 3376 (2000).
- <sup>5</sup>Q. Lin, R. Sooriyakumaran, and W.-S. Huang, *Proc. SPIE* **3999**, 230 (2000).
- <sup>6</sup>G. M. Wallraff and W. D. Hinsberg, *Chem. Rev.* **99**, 1801 (1999).
- <sup>7</sup>D. D. Y. Ryu and D. H. Nam, *Biotechnol. Prog.* **16**, 2 (2000).
- <sup>8</sup>A. K. Ghose, V. N. Viswanadhan, and J. J. Wendoloski, *J. Comb. Chem.* **1**, 55 (1999).
- <sup>9</sup>J. C. Meredith, A. Karim, and E. J. Amis, *Macromolecules* **33**, 5760 (2000).
- <sup>10</sup>J. C. Meredith, A. P. Smith, A. Karim, and E. J. Amis, *Macromolecules* **33**, 9747 (2000).
- <sup>11</sup>G. M. Wallraff *et al.*, *SPE Proceedings of the 12th International Conference on Photopolymers*, McAfee, NJ, 2000, p. 375.
- <sup>12</sup>Commercial equipment and materials are identified in this article only to adequately specify experimental procedure. In no case does this imply endorsement or recommendation by the National Institute of Standards and Technology.
- <sup>13</sup>S. Tanimura, T. Kumada, A. Ueyama, J. Kobayashi, and K. Kuramoto, *Appl. Spectrosc.* **51**, 1352 (1997).
- <sup>14</sup>G. Wallraff, J. Hutchinson, W. Hinsberg, F. Houle, P. Seidel, R. Johnson, and W. Oldham, *J. Vac. Sci. Technol. B* **12**, 3857 (1994).
- <sup>15</sup>H. Ito, *J. Polym. Sci. A* **24**, 2971 (1986).
- <sup>16</sup>J. M. Frechet, E. Eichler, H. Ito, and C. G. Willson, *Polymer* **24**, 995 (1983).
- <sup>17</sup>G. Wallraff, J. Hutchinson, W. Hinsberg, F. Houle, and P. Seidel, *Microelectron. Eng.* **27**, 397 (1995).
- <sup>18</sup>S. Burns, M. D. Stewart, J. N. Hilfiker, R. A. Synowiki, G. M. Schmid, C. D. Brodsky, and C. G. Willson, *SPE Proceedings of the 12th International Conference on Photopolymers*, McAfee, NJ, 2001, p. 323.