A Fundamental Study on Dissolution Behavior of High-Resolution Molecular Glass Photoresists

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Understanding the dissolution behavior of photoresist materials is an important step in being able to control their lithographic performance. In this paper, we present a fundamental study of dissolution behavior of a new type of photoresist based on molecular glasses (MGs). This study focuses on MG resists derived from a phenolic functionality similar to poly(4-hydroxystyrene), but designed with different types of branched and ring architecture that grant amorphous character. The work describes the unique dissolution behavior of MGs in aqueous base developer and evaluates the effect of molecular structure on their dissolution properties. In this study, we compare the dissolution behavior of two types of positive tone MG resists, ring and branched architectures. We have monitored their dissolution as deprotection takes place converting the resist materials from base insoluble to base soluble. The protection level of each MG system is probed in detail to identify where the solubility switch occurs and to understand the structural effects that govern swelling and dissolution behavior. We have found that the hydrophobic nature of the resist film surface causes severe swelling before dissolution in branched MGs. But the increase in hydrophilicity of the ring MG system is identified as the main reason for its smooth transition from insoluble to soluble in aqueous developer without swelling and with improved resist contrast. The effect of processing conditions such as post exposure bake (PEB) temperature and developer concentration have been evaluated as a means of controlling the swelling behavior in branched MG resists.

Introduction

The drive toward smaller dimensions in feature sizes has led to the development of new lithography technologies that employ increasingly shorter wavelengths.[1] The first important development that allowed the patterning of submicrometer features was the introduction of a positive tone photoresist composed of diazonaphthoquinones (DNQs) and novolac-based resins for g-line (436 nm) exposures.[2] Since then, the industry has advanced to deep UV wavelengths such as 248 and 193 nm employing the chemical amplification technology most likely to be extended to next generation lithography.[3] In chemical amplification, a photoinitiated acid catalyst is used that can initiate hundreds of chemical reactions to convert an optical image to a latent image through a thermally activated reaction diffusion process.[4] This chemical change gives rise to significant differences in dissolution rates between the exposed and unexposed regions. Resolving these features depends on the change in photoresist solubility over a narrow range of chemical compositions controlled through the acid-catalyzed chemical reaction during the imaging process.

The response of chemically altered photoresists upon exposure to a base developer varies significantly with the molecular structure and chemistry of the photoresist. Because of the complex nature of the dissolution process, numerous approaches have been taken to understand photoresist polymer dissolution through the application of various models. The dissolution of the novolak−DNQ system has been explained through several well-known theories such as the membrane model,[5] stone wall model,[6] percolation model,[7,8] and critical ionization model.[9,10] Previous studies have shown that the workhorse of the industry for many decades, novolac-based photoresist systems, dissolve in the current photoresist developer, 0.26 N tetramethylammonium hydroxide (TMAH) solutions, with minimal swelling.[2] Dur-

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ing this process, the base developer ionizes the acidic phenolic groups and dissolves the resin in the exposed areas. Interestingly, even as the industry moved on to shorter wavelengths, 0.26 N TMAH developer originally optimized for the novolac/diazoquinone resist system has been imposed on new resist systems built on very different polymer backbones. Although novolac and poly(4-hydroxystyrene) (PHOST) are both phenolic polymers, PHOST dissolves in aqueous base at a substantially higher rate.[10,11] The response of these photoresist materials to the base developer has been found to be dependent on polymer molecular weight, polydispersity, and developer concentration.[9] Such differences encountered in the transition to new photoresist platforms necessitate the investigation of dissolution kinetics in aqueous base. This type of understanding enables the design of high-resolution resist materials with the ability to control the development process through chemistry and processing conditions.

As the industry explores emerging technologies such as immersion lithography, extreme ultraviolet lithography (EUVL) and electron-beam (e-beam) lithography, new types of photoresists are also being considered. Photoresists based on small organic molecules known as "molecular glasses" (MGs) have gained increased attention in recent years.[12−14] MG photoresists are low molecular weight organic molecules that combine the beneficial properties of both small molecules and polymers. MGs are discrete small molecules that can be repeatedly synthesized with precise molecular structure with monodisperse molecular weight distributions.[15,16] Despite their small size, MGs possess structural features that inhibit crystallization, display high glass transition temperatures (T_g's) and form stable thin films. Molecular shape is a dominant factor in the glass forming ability of molecular systems. Common glass forming topologies include branched or star shapes,[17,18] ring structures,[19−21] spiro links,[22,23] tetrahedral,[24] and twin[25] molecular structures. Our previous work has demonstrated that ring molecules such as calyx[4] resorcinarenes[13,20] which exist in a mixture of isomers or branched bulky architecture[26,27] are conducive to forming high T_g molecular structures with modest molecular weights. We have focused on representative resist structures of both ring and branched architecture in this study to understand the role of molecular architecture on photoresist dissolution.

With feature sizes moving to 32 nm and below, MG resists are considered as a possible replacement for traditional polymeric resists. The small size of the imaging building block in MG resists is expected to result in a fundamental reduction of the "pixel size" compared to conventional polymeric resists. The reduction in the molecular size of the resist matrix is also thought to lead to several other advantages, including a decrease in pattern fluctuations known as line edge roughness (LER) and a superior component miscibility with small molecule additives. Recent published work highlights several MG photoresist systems that are able to attain sub-50 nm resolution with improved resist performance.[13,26−28] Additionally, the development of MG photoresists has been supported by theoretical work that shows how photoresist performance improves with the reduction of molecular weight of the resist, for both classical and chemically amplified photoresists.[29−31] The ability to control dissolution behavior during the development process through resist architecture is considered to be another advantage of pursuing the MG resist platform.

The impact of small size and monodispersity of MGs on resist properties such as resolution, surface roughness and LER has been studied through theory and experiments to evaluate its merits. However, the structural effect of MGs on its dissolution behavior has not yet been understood. Varied responses of different polymers to developer solutions indicate that significant changes in dissolution rate and development contrast may occur upon changing the resist matrix to MG photoresists. This paper presents a detailed study of dissolution properties of MG photoresists in aqueous base. Phenolic MGs have been compared with PHOST based polymers to evaluate the effect of size and establish the unique dissolution properties of MGs. Structural features that affect dissolution in MG resists, such as molecular size, rigidity, and hydrophobicity have also been identified. This paper also explores the effect of developer concentration, which is identified as a key parameter that control dissolution rate of MG photoresists. Two types of MG platforms based on ring and branched architectures were studied to compare their resist performance on the basis of dissolution behavior. The dissolution behavior of these positive tone MG systems has been studied in detail to understand how the dissolution changes with *tert*-butoxycarbonyl (*t*-BOC) deprotection.

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Experimental Section

Materials. Chemicals were purchased from Sigma-Aldrich unless otherwise stated and used without further purification. Anhydrous or HPLC grade solvents were used unless otherwise stated. Commercially available CD-26 was employed as a standard developer (0.26 N tetramethylammonium (TMAH) hydroxide in water).

Synthesis of Phenolic Molecular Glass Resists. The phenolic MGs CR8-17 were synthesized from an acid catalyzed condensation of phenol with the respective aldehyde or ketone in the presence of hydrochloric and acetic acid.[26] The compounds were obtained in relatively moderate yields after careful purification with a combination of solvent mixtures.

The calix[4]resorcinarene derivatives were synthesized through an acid catalyzed one-pot reaction between resorcinol and the respective aldehydes.[20] They were obtained in high yields as a mixture of various isomers and used without further purification.

These compounds were protected with *t*-BOC to varying degrees by a standard base-catalyzed reaction in the presence of 4-dimethylaminopyridine (DMAP).[32] To obtain very pure samples, we subsequently subjected partially protected compounds to column chromatography with acetone as the eluent. 100% *t*-BOC protected samples were purified using dichloromethane as the eluent.

Measurements. ^{1}H NMR spectra were recorded on a Varian Inova-400 (400 MHz) at room temperature, using the chemical shift of a residual hydrogen in deuterated solvent ($CHCl_3$ at δ 7.28 ppm, acetone at 2.05 ppm, or dimethyl suloxide (DMSO) at δ 2.50 ppm) as an internal reference. Thermogravimetric analysis (TGA) was performed on a TA Instruments Q500 at a heating rate of 10 °C/min under N_2. The glass transition temperatures (T_g) of resist materials were measured on a TA Instruments Q1000 Modulated differential scanning calorimeter (DSC) at a heat/cool rate of 10 °C/min under N_2 for three heat/cool cycles. T_g was determined on the second heating cycle. Scanning electron micrographs (SEMs) were taken on Zeiss Ultra 55 scanning electron microscope.

Dissolution kinetics were followed by a quartz crystal microbalance (QCM) setup with a Maxtek Inc. (recently a part of INFICON) CHC-100 crystal holder and a PLO-10 phase lock oscillator used in conjunction with a Phillips PM6654 programmable high resolution frequency counter. The instrumentation was controlled from a PC and data were collected by a custom-made LabView software program. The upper limit of the data density was 200 points/s, which allowed us to follow extremely fast dissolution. Five megahertz quartz crystals with gold electrodes were spin coated with the thin resist films (typically in the range of 120−160 nm) and thermally processed with post apply bake (PAB), exposure at 254 nm UV light (if needed) and post exposure bake (PEB) conditions before being mounted on the crystal holder with sensor probe. Through this technique, any changes in mass that occur for various reasons such as sorption of the developer or removal of the resist film are detected as changes in the resonance frequency of the piezoelectric crystal. The change in frequency is directly proportional to the mass change of the crystal according to the Sauerbrey equation (eq 1).[33] The measured changes in frequency were converted to changes in film thickness using Sauerbrey's equation in our analysis. The QCM method shows high sensitivity, on the order of nanograms.

$$\Delta F = -\frac{2f_0^2}{A\sqrt{\rho_q \mu_q}}\Delta m \quad (1)$$

where ΔF = frequency change, f_0 = resonant frequency (Hz), A = area, ρ_q = quartz density (2.648 g/cm^3), μ_q = quartz shear modulus (2.947 × 10^{11} g/(cm^2 s^2)), and Δm = mass change.

Table 1. Blends of CR15 and CR15-50; Blends of C-M-4-R and C-M-4-R-75

blends	CR 15 (mg)	CR15−50 (mg)	% protection
1	0	30	50
2	5	30	41
3	10	30	33
4	15	30	30
5	20	30	25
6	30	30	21
7	30	0	0

blends	C4 (mg)	C4−75 (mg)	% protection
1	0	30	75
2	2.5	30	64
3	5	30	56
4	7.5	30	50
5	10	30	44
6	15	30	38
7	20	30	31
8	25	30	27
9	30	30	24
10	30	0	0

Lithographic Processing of Positive-Tone MG Resists. The resist compounds were dissolved in propylene glycol methyl ether acetate (PGMEA) making a 5 wt % solution. A commercially available PAG, triphenylsulfonium perfluoro-1-butanesulfonate (5 wt % with respect to resist) was used unless otherwise stated. The MG solution was filtered through a 0.2 μm membrane filter and spin coated on to a QCM wafer at 1200 rpm for 30 s to form thin films in the thickness range of 120−160 nm. The films were flood exposed at various doses at 254 nm.

CR15-50 and C-M-4-R-75 phenolic MG resists were evaluated through EUV exposure at Lawrence Berkeley National Laboratory (LBNL).

Preparation of MG Blends. MGs with varying amounts of protection were prepared by blending the unprotected MGs with partially protected MGs according to the ratios displayed in Table 1. For branched MGs, CR15 and CR15-50 (50% t-BOC protected CR15) and for ring MGs, C-M-4-R and C-M-4-R-75 (75% t-BOC protected C-M-4-R) were chosen as the systems for investigation. The blends were dissolved in PGMEA at 5 wt % and mixed at room temperature overnight to ensure complete miscibility.

Results and Discussion

We have used a quartz crystal microbalance (QCM) to study the dissolution and swelling behavior of resist thin films in aqueous TMAH solution.[34] The results are divided into a few sections: first, we discuss dissolution of unprotected MGs describing not only effect of MG structure but also developer concentration effects on dissolution properties. Thereafter, we present the dissolution result of partially protected MGs using three different techniques.

Dissolution Behavior of Phenolic-Based Unprotected MG Systems. Several MG systems of two different types of molecular architecture (branched and ring) in a range of molecular weights (500−1000 g/mol) were studied to understand the structural effects on the dissolution behavior of these resist systems (Figure 1). As a comparison, two different types of PHOST polymers of varying MWs have

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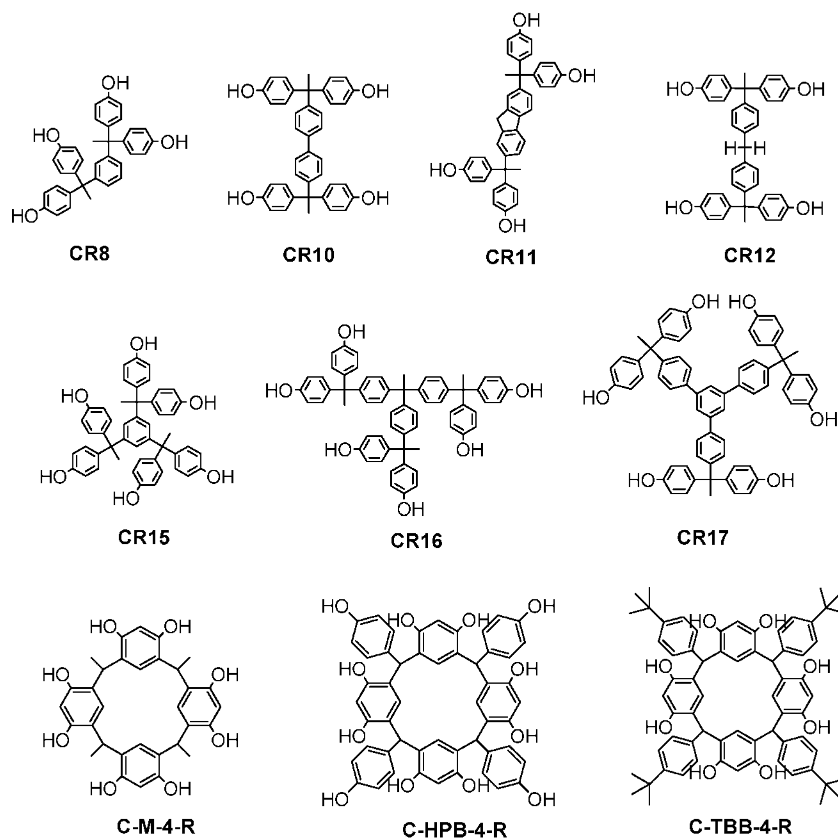

Figure 1. MGs of branched and ring architecture.

Table 2. Molecular Structure and Dissolution Rate Correlation for Several Phenolic MGs

MG type	mol wt (g/mol)	unprotected T_g (°C)	C/O ratio	unprotected dissolution rate (nm/s)
		Branched-MGs		
CR8	502.6	100	6.38	3730
CR10	578.7	129	7.51	3322
CR11	590.71	107	7.7	5581
CR12	592.72	117	7.69	5604
CR15	714.84	126	6	4558
CR16	895.09	130	7.76	212
CR17	943.13	165	8.26	197
		Ring-MGs		
C-M-4-R	544.59	84	3	4780
C-HPB-4-R	856.87	157	3.25	5140
C-TBB-4-R	1017.29	110	6.38	160
		Polymers		
PHOST (5k)	5000	N/A	6	463
PHOST (8k)	8000	135−180	6	397

been included. It is important to note that in terms of molecular weight, MGs are an order of magnitude lower molecular weight compared to conventional polymeric photoresists. Table 2 shows the dissolution rates of several phenolic MG systems in the standard aqueous base developer (0.26N TMAH). Similar to the already established dissolution behavior of PHOST, MGs also displayed linear dissolution behavior and dissolved at constant rates.[11] However, except for the largest MGs in each type of architecture (CR16 and CR17 for branched, C-TBB-4-R for ring), all other MGs developed within 0.2s, at very fast dissolution rates greater than 3000nm/s. This behavior can be compared to the low-molecular-weight novolac fractions in a previous study that developed so fast that reliable rate measurements were not possible.[35] Most MGs considered in this study demonstrate dissolution rates at least 1 order of magnitude higher compared to the PHOST samples.

It has been found that dissolution rates of PHOST can be predicted from M_n regardless of M_w or polydispersity, and their observation suggests that the dissolution rate of PHOST in aqueous base is governed primarily by the lower-molecular-weight fractions.[11] A similar study was conducted on cresol novolac resins concludes that the dissolution rate is highly dependent on M_w and polydispersity and that the rate is more strongly influenced by the higher-molecular-weight components of the distribution.[35] This illustrates that though molecular weight is a significant factor, each resist platform has a different type of mechanism that controls dissolution in aqueous base. Though increasing molecular size seems to significantly decrease the dissolution rate in MG resist systems, M_w may not be the only factor that affects dissolution.

Because of the bulky dense structure inherent to glass forming molecules hydrophobicity also plays an important role in defining molecular performance of MG resists. The ratio of carbon to oxygen (denoted as C/O) in the resist systems has been utilized as a rough measure of hydrophobicity of MG resists based on its atomic composition. It can be noted that the MG resists that have significantly low dissolution rates also have relatively high C/O ratios in

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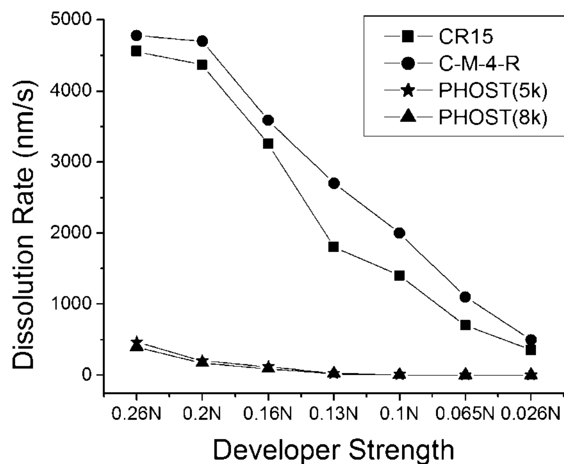

Figure 2. Dissolution rates of MGs (CR15 and C-M-4-R) and PHOST samples in varying developer concentrations.

addition to high M_w values. Hence, the dissolution in MGs with rigid aromatic core structures such as CR16 and CR17, and bulky tert-butyl substituents such as C-TBB-4-R, is significantly affected by the hydrophobicity of the molecule despite only a modest increase in molecular weight. This observation highlights the relationship between molecular architecture and dissolution behavior for MG photoresists. Hence, the effects of molecular size and structure can be used to predict dissolution behavior of phenolic MG resists.

Dissolution Behavior of MGs with Decreasing Developer Concentration. The dissolution of MGs and PHOST samples were investigated in a range of developer concentrations from 0.26 to 0.026 N TMAH (Figure 2). Similar to previous studies conducted on novolac-DNQ systems,[35] we found that the dissolution rates of MGs and PHOST were strongly dependent on developer concentration.

Because of the very fast dissolution of MGs, no significant change can be observed until the developer concentration has been reduced to 0.16N. Only a slight variation is observed for the dissolution rate values for developer concentrations in the range of 0.26−0.2 N. But in the developer concentration range from 0.16 to 0.026 N, the dissolution rates of studied MGs change linearly with concentration. The PHOST samples demonstrate comparable dissolution rates with PHOST (5k), being slightly faster than PHOST (8k) because of lower molecular weight. This agrees with previous reports where molecular weight of PHOST has been identified as an important parameter that controls dissolution in aqueous base.[11] It is interesting to note that the dissolution rate of MGs at 0.026N is the same order of magnitude as that of PHOST samples at 0.26N. The dissolution of PHOST systems also decreases linearly with dilute developer but at a much slower rate compared to MGs. At the two lowest concentrations (0.065 N & 0.026 N), PHOST samples do not dissolve but swell significantly.

The distinct difference between the dissolution behavior of our selected MGs and PHOST due to developer strength may be explained in terms of molecular size. As discussed in detail later in this section, for a MG system, only a few functional groups need to be ionized to render the molecule soluble in aqueous base. But the number of phenolic units that need to be ionized to enable PHOST dissolution is much higher, thus decreasing the dissolution rate significantly. Therefore, even if PHOST has a similar C/O ratio to CR15 and similar phenolic functionality, the change in molecular size gives rise to different dissolution behavior. The role of molecular structure on dissolution behavior can be understood through the comparison of CR15 and C-M-4-R. Because of the increased number of phenolic groups as well as the low C/O ratio, C-M-4-R maintains a higher dissolution rate compared to CR15 even at dilute developer concentrations. This study indicates that a wide range of developer concentrations can be explored through MG resists, as the dissolution rate can be fine-tuned by changing developer concentration.

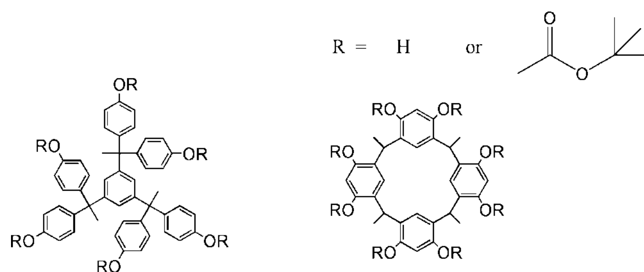

Figure 3. Partially t-BOC-protected structures of branched CR15 and ring C-M-4-R.

Dissolution Behavior of Positive Tone MG Resists after Deprotection. After understanding the dissolution properties of the unprotected MGs, the dissolution of the MG resists at various levels of t-BOC deprotection needs to be established. The t-BOC deprotection step that occurs due to the sinusoidal aerial image of the exposing radiation needs to be converted to step function in the resist film during the development process.[36,37] High development contrast of a photoresist is an important parameter that enables improved lithographic performance through reduced surface roughening and LER.[38] Hence, the dissolution properties of MGs as a function of t-BOC protection are studied for two different model systems. CR15 and C-M-4-R (Figure 3) have been chosen as the model systems as they have been previously studied for their thermal and lithographic properties. Both MG systems have demonstrated high-resolution capability by producing sub 30 nm feature sizes with EUV exposure (Figure 4).

When MGs are converted to positive tone resists, the optimal protection ratio of each protecting group for a particular MG core must be optimized. We determined our most favorable t-BOC protection by the number of protecting groups needed to prevent dissolution of unexposed regions in developer solution (dark loss) as well as provide high sensitivity upon exposure to radiation. Because of the small size and large number of phenolic moieties present, MGs need a relatively high level of protection when compared to polymeric samples. The typical protection level of an APEX type photoresist which is based on partially t-BOC-protected PHOST is about 25−33%. But for most t-BOC-protected

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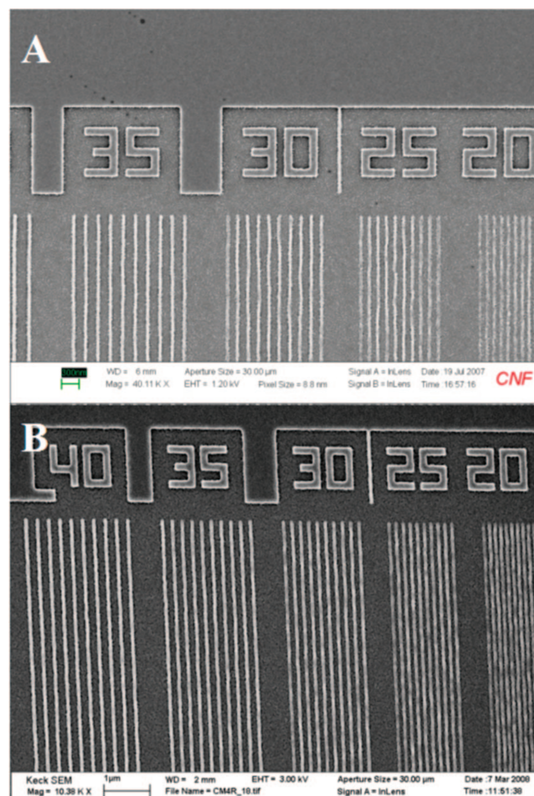

Figure 4. SEM images from EUV exposures of (a) CR15-50 and (b) C-M-4-R-75.

MG resist systems the protection level is greater than 50%. For the model systems considered in this study the t-BOC protections vary from 50% for CR15 (CR15-50) to 75% for C-M-4-R (C-M-4-R-75). This difference in protection levels can be attributed some inherent differences in their molecular structure. Though C-M-4-R is smaller in size than CR15, it has nearly double the number of hydroxyl groups with respect to aromatic functionality. The decrease in C/O ratio results in increased hydrophilicity that translates to high dissolution ability in aqueous base developer. This part of the study focuses on understanding the changes in dissolution behavior of different t-BOC protection content.

The lower protection levels for each system have been probed using three different methods to yield consistent results.

1. The various levels of t-BOC-protected samples were prepared through careful synthesis procedures. The t-BOC protection level was determined by TGA analysis to evaluate the average t-BOC protection in the resist system.

2. Low protection ratios were probed through blends of high t-BOC-protected samples with unprotected MGs in various ratios.

3. Increasing exposure dose is expected to reduce t-BOC protection as more photo acid is generated with higher dose. Hence, the dissolution properties at low doses that correspond to low t-BOC-protected materials were analyzed.

Results from these studies were compared and depicted in Figures 5a−c and 6a−c.

Dissolution Behavior of CR15 with Increasing Deprotection. Figure 5a shows the dissolution behavior of various CR15 with increasing levels of protection. No change in thickness is observed at protection levels of 50% or above, indicating no dark loss in the unexposed regions when at least 3 hydroxyl groups are protected with t-BOC. But as the level of deprotection decreases to 35%, corresponding to about two phenolic groups being protected with t-BOC, severe swelling followed by dissolution is observed. Permeation of developer solvent in to the thin film results in a mass increase that can be observed as an increase in thickness. Similar to certain polymeric resists parallel behavior is seen in the resistance response as well. The increase in thickness due to the swelling is followed by a resistance shift. This change in resistance indicates a significant change in physical properties of the film. Dissolution of the films proceeds very slowly as the MGs are dissolved from the swollen matrix. When the deprotection decreases further (20% and below) leaving only one hydroxyl group protected, the respective film dissolves very fast, with no swelling at a rate comparative to that of the unprotected MG.

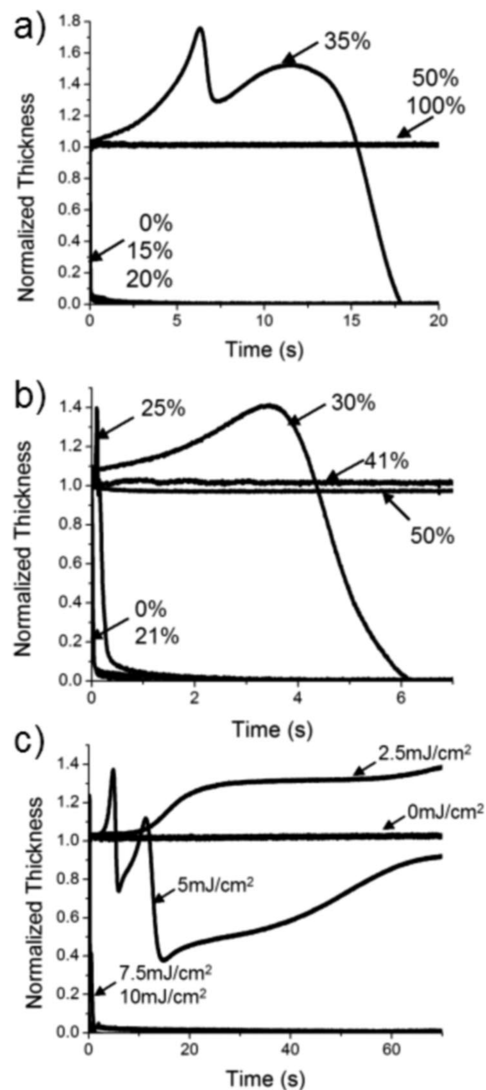

Figure 5. (a) Dissolution of CR15 samples of varying protection levels, prepared through synthesis; (b) dissolution of CR15 blends of varying protection levels; (c) dissolution of CR15-50 with increasing dose.

This behavior is further confirmed by studying the blends of CR15 and CR15-50 to yield samples in the lower

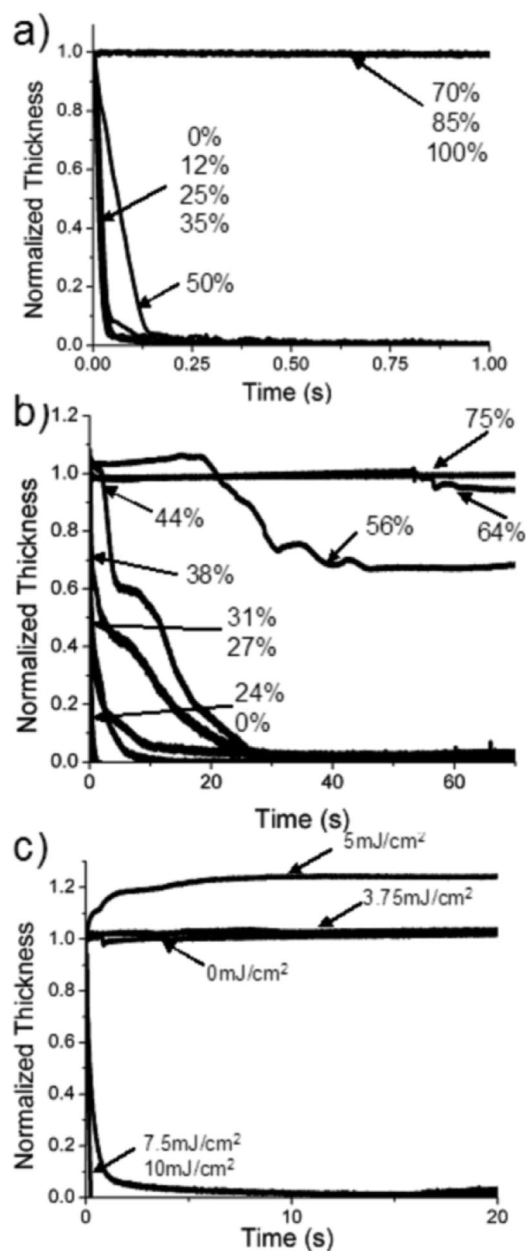

Figure 6. (a) Dissolution of C-M-4-R samples of varying protection levels; (b) dissolution of C-M-4-R blends of varying protection levels; (c) dissolution of C-M-4-R-75 with increasing dose.

protection regime (Figure 5b). Similar to the behavior of novolac blends, the dissolution rates of MG blends falls between that of the two components that constitute the particular blend. Swelling behavior is observed when the protection level is 30% but fast dissolution is observed as deprotection level decreases to <30%. This clearly indicates that the average protection level of the MG system has a strong influence on its dissolution behavior.

We also investigated the dissolution response of the MG resist films to an aqueous base solution as a function of the average protection level as it changes during an acid-catalyzed deprotection reaction (Figure 5c). In order to understand how the deprotection occurs in presence of PAG and exposure @ 254 nm UV light. At low doses, the generation of the photoacid and deprotection is expected to be limited. Film swelling and partial dissolution can be observed at the low doses between 2.5−3.75 mJ/cm^2. The previous studies indicate that this behavior corresponds to a protection level of 30−35% in the MG system. But upon increasing the dose, more deprotection takes place and fast dissolution is observed.

Dissolution Bhavior of C-M-4-R-75 with Increasing Deprotection. A similar study was conducted for a MG with ring structure in order to compare and contrast its dissolution behavior with that of the branched system described earlier. Figure 6a shows the dissolution behavior of various C-M-4-R with increasing levels of protection. When the t-BOC protection level is greater than 50% no dissolution is observed. But when the deprotection level is 50% or less, dissolution in aqueous base occurs. In the C-M-4-R MG system at least four hydroxyl groups need to be protected to prevent dissolution. The rate of dissolution increases with decreasing levels of protection as expected. Several blends of C-M-4-R and C-M-4-R-75 were mixed in various ratios to result in a range of t-BOC-protected samples below 75%. Figure 6b shows that C-M-4-R-56 undergoes some dissolution but no dissolution is observed at C-M-4-R-64 confirming the results from Figure 6a that for the C-M-4-R MG system an average of 50% t-BOC, results in dissolution without any swelling behavior. The deprotection of C-M-4-R-75 is also monitored with increasing dose (Figure 6c). The thin film swells around a dose of 5 mJ/cm^2, but fast dissolution is observed at higher doses. This result indicates that doses greater than 5 mJ/cm^2 at 254 nm UV exposure are needed to deprotect at least 50% of the MG system.

Both MG resists considered in this study do not swell or undergo dark loss in their optimized protection ratios. Upon complete deprotection, these films dissolve quickly in the aqueous developer solution. However, it is the difference of the dissolution behavior in their intermediate protection levels that distinguishes these two systems based on their molecular structure. This type of fundamental study highlights structural factors that need to be considered with respect to resist dissolution that controls lithographic performance.

Though "mild" swelling in comparison with massive swelling observed with carboxylic acid polymers and partially protected CR15 samples, was observed for C-M-4-R-75 at 5 mJ/cm^2, no swelling behavior was observed when lower protection samples were analyzed.[39] This indicates that at lower protection ratios C-M-4-R MG system are not prone to severe swelling compared to thin films of CR15. This behavior can be correlated to the inherent properties of molecular structure in these two resist systems. C-M-4-R has nearly double the number of hydroxyl groups per aromatic ring compared to CR15. This change in hydrophilicity gives rise to the change in dissolution behavior observed at lower protection ratios. Around 50−60% protection when the solubility switch occurs in the C-M-4-R system, there are sufficient hydroxyl groups that can be converted to polyanions and enable subsequent dissolution in aqueous base. The hydrophilic character in C-M-4-R ensures dissolution with either mild or no swelling behavior as the developer is able to permeate through the film and dissolve it very fast because

(39) Hinsberg, W.; Houle, F. A.; Lee, S. W.; Ito, H. *Macromolecules* **2005**, *38*, 1882.

of hydroxyl groups distributed throughout the film. Hence, the ring system demonstrates higher development contrast that may result in improved lithographic properties such as low LER.

However, CR15 is less hydrophilic than C-M-4-R in comparison. At around 30−35% protection, the MG resist molecules are too hydrophobic to be rendered soluble in aqueous developer but are sufficiently hydrophilic to swell. The hydroxyl groups can form a percolated network that provides a pathway for the transport of base developer into the film thereby resulting in film swelling. When the deprotection level decreases further, there is sufficient hydrophilicity in the film that can enable film dissolution without swelling. This type of behavior has been observed for methacrylic-based 193 nm photoresists where swelling occurs upon initial deprotection but yields to complete dissolution after further reaction.[40]

Effect of Processing Conditions on Swelling Behavior. This phenomenon of swelling at the line edge where the dose and thereby the protection ratio may be at the solubility switching range may have a significant effect on LER. Hence, we need to gain a clearer understanding of the factors that control swelling in order to prevent swelling and improve resist contrast during development. To avoid swelling in the CR15 MG system, we took two different approaches to evaluate the effects of processing conditions. First, the PEB temperature was increased from 80 to 90 °C to ensure higher levels of deprotection at similar dose levels. As Figure 7a indicates, complete dissolution occurs with no swelling at a dose of 5mJ/cm^2 in contrast to the dissolution behavior of the same dose at PEB = 80 °C (Figure 5c). This indicates that by increasing the PEB a higher level of deprotection has been obtained in the system at this particular dose level. However, swelling can still be observed at doses less than 5mJ/cm^2, where sufficient deprotection has not taken place. This study illustrates how the different responses of the MG film to the developer solution are a consequence of the relative hydrophobic-hydrophilic nature of the resist film. This also gives us insight to the levels of deprotection we need for each system to ensure dissolution at a specific dissolution rate.

In the second approach, the developer was changed to 0.13 N TMAH, which is at half the strength of the regular developer. From the study of dissolution of MGs with decreasing developer, we understand that rate of dissolution will be significantly affected by switching to the dilute developer (Figure 2). Figure 7b indicates that the decrease in dissolution rates is even more pronounced at low t-BOC protection levels, as no dissolution is observed up to a dose of 10 mJ/cm^2. At a dose of 15 mJ/cm^2, slight swelling occurs because of the permeation of developer into the resist film, but the developer was not strong enough to carry out dissolution. Increasing the dose further enables dissolution at much slower rates relative to the standard developer. This result indicates that severe swelling may not occur under dilute conditions as the developer is too weak to penetrate the resist film at deprotection levels of 30−35% that are susceptible to swelling. Higher levels of deprotection that allow the developer to penetrate will prevent severe swelling due to the hydrophilic character. Dissolution will occur at higher doses that give rise to higher levels of deprotection and relatively lower dissolution rates compared to the standard developer.

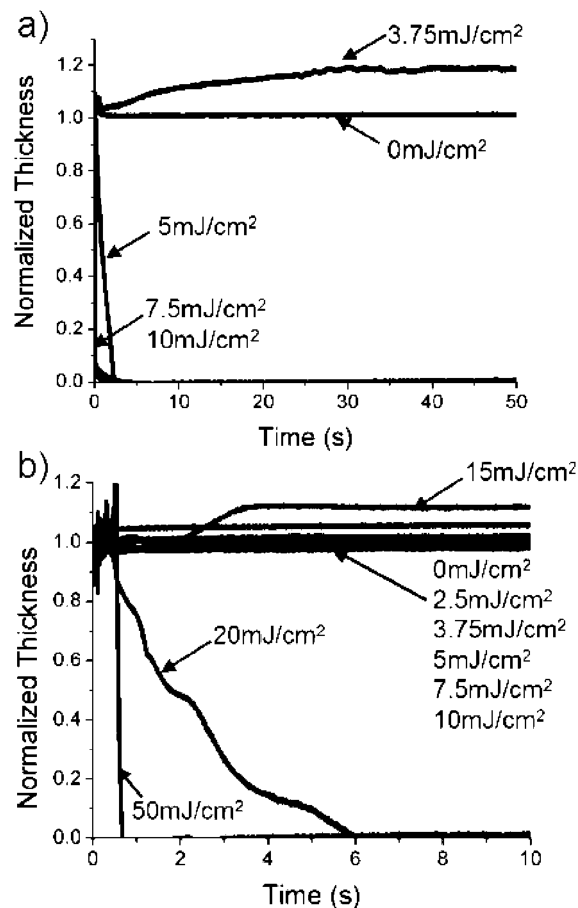

Figure 7. (a) Dissolution of CR15-50 with increasing dose, PEB = 90 °C/30 s; (b) dissolution of CR15-50 with increasing dose, developer strength 0.13N TMAH.

Conclusion

This paper presents a detailed study of dissolution behavior of MG photoresists. Several phenolic MGs have been investigated to establish the unique dissolution properties of small molecule resists. Although most MGs considered in this study dissolve extremely fast in aqueous base developer compared to phenolic polymers, modifications to the resist structure through increase in size, rigidity, and hydrophobicity can significantly alter their dissolution rates. Studies conducted with varying developer concentrations show that dissolution rate of MGs can be controlled by developer strength, and swelling can be mitigated. The differences in dissolution behavior between ring and branched architectures have also been evaluated by understanding the dissolution behavior as a function of t-BOC deprotection composition. The relative hydrophilicity of the MG systems has been identified as a strong influence that determines swelling behavior and dissolution rates. The branched CR15 system undergoes severe swelling as a result of insufficient hydrophilic character at the solubility switching t-BOC protection

(40) Rao, A.; Kang, S.; Vogt, B. D.; Prabhu, V. M.; Lin, E. K.; Wu, W.-L.; Muthukumar, M. *Langmuir* **2006**, *22*, 10009.

level. However, when the hydrophilicity is increased, through additional phenolic groups as in the C-M-4-R ring system, the swelling behavior can be mitigated while high development contrast is observed.

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