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High sensitivity nonchemically amplified molecular resists based on photosensitive dissolution inhibitors

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A new class of nonchemically amplified molecular resists has been made based on the use of photosensitive protecting groups. The deprotection during exposure converts a dissolution inhibiting compound into a dissolution promoter. The key benefit of the use of molecular resists in this application is that they can exhibit a sharp solubility transition with relatively low levels of deprotection. Two different inhibiting compounds were made that use a 2-nitrobenzyl protecting group; NBnDCh, an aliphatic molecular resist based on deoxycholic acid, and NBnHPF, based on an aromatic molecular resist containing two phenol groups. Blending these compounds with a calixarene dissolution promoter allowed the contrast and sensitivity of the resist formulations to be tuned. Contrast ratios as high as 27 and deep ultraviolet (DUV) sensitivities between 150 and 400 mJ/cm^2 were obtained using NBnDCh. NBnHPF based systems not only showed somewhat lower contrasts but also exhibited much lower clearing doses of only 60 mJ/cm^2 and smaller. One particular NBnHPF formulation possessed a sensitivity of 10 mJ/cm^2 and a contrast of 8.3, and it was even possible to formulate one resist with an extremely low dose-to-clear value of only 1 mJ/cm^2. Such low dose-to-clear values in nonchemically amplified resists have, to the authors' knowledge, not been reported before. The Dill C parameter for each of the two systems was quantified using Fourier transform infrared spectroscopy. The sensitivity of the NBnHPF systems was found to be very good because they undergo a solubility transition at 75 mol % inhibitor; this means that some formulations only need 0.5% photoconversion to pattern. Despite the excellent DUV sensitivity of these systems, it was found that they do not possess high sensitivity when exposed using extreme ultraviolet or e-beam exposure sources. © *2010 American Vacuum Society.* [DOI: 10.1116/1.3511790]

I. INTRODUCTION

Chemically amplified resists (CARs) have formed the workhorse material for commercial submicrometer deep ultraviolet (DUV) lithography using both KrF and ArF lasers and will likely be the resists used for the initial commercialization of extreme ultraviolet (EUV) lithography. In large part, this is due to the generally accepted premise that CARs offer significantly improved sensitivity compared with nonchemically amplified resists (non-CARs). This sensitivity improvement is because non-CARs typically undergo a single reaction per photon (at DUV) often accompanied by a relatively low quantum yield. In CARs, a single photon can produce a photoacid that can catalytically carry out multiple additional reactions; thus, the required number of photons, or dose, to effect an equivalent solubility change is greatly reduced in CARs.

Unfortunately, the photoacid, which gives CARs superior sensitivity, also reduces their resolution due to diffusion of the photoacid outside of the exposed region during the postexposure bake (PEB). Since all the reactions in non-CARs typically occur during exposure, they can avoid this diffusion blur and have superior resolution. Likewise, the random walk nature of photoacid diffusion in CARs is especially apparent at these sub-50 nm length scales and can contribute to line edge roughness (LER) and line width roughness.[1] Despite steady improvements in the resolution of CARs, little progress has been made in the improvement of LER, and LER in current champion CARs still lags far behind the desired International Technology Roadmap for Semiconductors performance targets.[2] While non-CARs generally still display a small amount of LER, it is typically much lower than that seen in CARs.[3,4] If non-CARs could achieve patterning at equivalent doses to CARs, they would likely be the preferred resist for high resolution patterning. Novel designs of non-CARs were thus investigated in this

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work in an attempt to greatly improve their sensitivity and thus yield a superior class of materials for future high resolution patterning.

While a number of studies have been done using polymeric nonchemically amplified resists,[5–8] much less work has been done using nonchemically amplified (non-CA) molecular resists. Molecular resists have several unique properties that can, in some cases, lead to substantial improvements over traditional polymeric resists. Most notably in molecular resists, their monodispersity, unique dissolution behavior, and very low molecular weight can produce significantly different behavior and patterning performance as compared with polymeric resist materials using similar imaging reactions and functional groups. For example, recent studies have shown that negative tone molecular resists based on epoxide cross-linking reactions show significantly improved performance compared with their polymeric analogs because of these unique properties.[9] The few negative tone non-CA molecular resists that have been studied, such as hydrogen silsesquioxane and several calixarenes,[10] showed excellent performance, but little work has been done on positive tone non-CA molecular resists. Most of the negative tone non-CA molecular resists that have demonstrated high resolution depend on stepwise cross-linking to form a less soluble network.[11,12] While such designs have been shown to provide high resolution, they also suffer from poor sensitivity because an electron or photon is required to effect nearly each individual molecular cross-linking event and nearly every molecule in the exposed area must be cross-linked to be rendered sufficiently insoluble. In contrast, the work presented here has focused on positive tone non-CA molecular resists that have large solubility changes in the resist matrix and the use of dissolution inhibitor motifs, which allow for a single reaction event to affect the solubility of several surrounding molecules rather than a single molecule. Furthermore, it was hypothesized that the unique dissolution properties of molecular resists should allow for higher contrast performance than in non-CA polymers because the transition from completely insoluble to completely soluble occurs over a very narrow range of compositional change in such molecular resist materials, especially in the ultrathin films that would be required for 22 nm patterning and below.

The venerable diazonaphthoquinone (DNQ)/novolak resists that use DNQ dissolution inhibitors form the workhorse materials for the 365 nm (*I*-line) wavelength lithography and above[13] because they have relatively good sensitivity and dissolution contrast. The good sensitivity of these systems is due to the DNQ, which acts to strongly inhibit the dissolution of novolak when unexposed, but acts as a dissolution promoter after exposure due to the Wolff rearrangement, which converts the DNQ to a carboxylic acid. Despite its excellent performance, when moving to the 248 nm lithography from the *I*-line wavelength, DNQ/novolak could not be used due to its high absorbance. Likewise, DNQ dissolution inhibitor based systems cannot be effectively used for positive tone resists under e-beam and EUV because the high vacuum in these systems removes the water required for the Wolff rearrangement from the resist film and the DNQ instead cross-links the matrix in such systems, resulting again in a negative tone behavior based on cross-linking.[14]

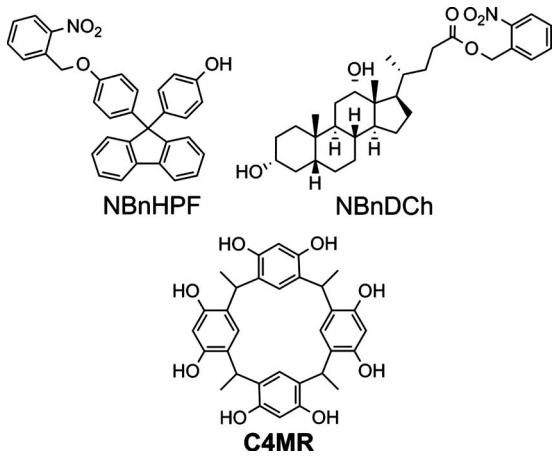

FIG. 1. Chemical structures of NBnHPF, NBnDCh, and C4MR.

To overcome this problem, dissolution inhibitors that use photosensitive protecting groups, which become dissolution promoters after photolysis without the requirement for water in a vacuum, were used in this work. The photosensitive protecting group can be put directly onto the molecular resist and it can act as its own inhibitor. Fortunately, much work has been done on photosensitive protecting groups for use in peptide and carbohydrate chemistries.[15] Resist designs of this type were even investigated at one time for use in early inhibitor based DUV polymer resists[16] before the widespread introduction and use of CARs. Since forms of photosensitive protecting groups are known to protect and release phenols, carboxylic acids, and sulfonic acids, they provide large versatility in potential resist designs.

The initial non-CA molecular resist designs explored using this approach contain a 2-nitrobenzyl (NBn) moiety as the photosensitive protecting group. It is one of the most widely known and examined photosensitive protecting groups.[17] The photochemical reaction mechanism has been shown to involve intramolecular insertion of an excited nitro group oxygen into a benzylic carbon-hydrogen bond followed by rearrangement to form nitrosobenzaldehyde and the unprotected alcohol or acid.[18] This mechanism is useful because it does not proceed through a radical bond cleavage that could lead to cross-linking, and neither does it require hydrogen abstraction from the surrounding molecules to complete the deprotection. The two photosensitive dissolution inhibitor compounds synthesized and studied here, NBnHPF and NBnDCh, are shown in Fig. 1 along with calix[4]resorcinarene (C4MR), which is added to formulations as a dissolution promoter. NBnDCh, 2-nitrobenzyl deoxycholate, has a nitrobenzyl (NBn) ester and forms a carboxylic acid functionalized molecular resist, i.e., a resist containing deoxycholic acid, upon photolysis. Deoxycholic acid was chosen instead of one of the many other bile acids, such as cholic acid or lithocholic acid, because its protected derivatives are reported to have better solubility[19] and to show

stronger interaction with carboxylic acids[20] than the derivatives of the other simple bile acids. NBnHPF, 9-(4-(2-nitrobenzyloxy)phenyl)-9-(4-hydroxyphenyl)-fluorene, has a NBn ether that forms a phenol after exposure. It was determined using an in-house solubility prediction model[21] that protecting only one of the two phenols on the starting core was sufficient to render the whole molecule insoluble in a standard developer. NBnHPF was purified by column chromatography to give only the pure monobenzylated molecular resist.

II. EXPERIMENT

A. Materials, equipment, and processing

All reagents and solvents used were purchased from either Sigma-Aldrich, TCI America, or Alfa-Aesar, and used as received. An aqueous solution of 0.26*N* tetramethylammonium hydroxide (AZ 300 MIF, AZ Electronic Materials) was used as developer. A Varian mercury Vx 300 was used to collect NMR. DUV exposures were done using an Oriel Instruments 500 W Hg–Xe arc lamp with a 248 nm bandpass filter. Film thicknesses were measured using an M-2000 spectroscopic ellipsometer (J. A. Woolam, Inc.) to collect ellipsometric spectra over the wavelength range from 350 to 1000 nm and by fitting these data using a Cauchy layer to determine the resist film thickness. Fourier transform infrared (FTIR) spectroscopy was done using a Bruker Vertex 80v with a Hyperion microscope attachment using a grazing angle objective for sub-100-nm thick films spin-coated onto gold coated silicon wafers. E-beam lithography was done using a JEOL JBX-9300FS electron-beam lithography system with 100 keV acceleration voltage, 2 nA current, and 10 nm single-pixel shot pitch. Resolution tests were done on resist films coated onto 46 nm thick silicon nitride membrane windows. The patterns produced by e-beam lithography were imaged using a Carl Zeiss Ultra60 scanning electron microscope with 3 keV acceleration voltage. EUV lithography was done using the Berkeley microfield exposure tool.

NBnHPF and NBnDCh were formulated with different mass fractions of C4MR, which acts like a dissolution promoter in this case. C4MR was synthesized as described elsewhere.[22] The mass fraction of C4MR in the formulations is specified by referring to the individual formulations as NAME.XX, where NAME specifies the dissolution inhibitor used (either NBnHPF and NBnDCh) and XX specifies the overall solids mass percentage of C4MR. For example, NBnHPF.10 contains 10% by mass C4MR and NBnDCh.20 contains 20% by mass C4MR. Four formulations of NBnHPF were made with 0%, 10%, 20%, and 25% C4MR, and four formulations of NBnDCh were made with 0%, 20%, 40%, and 50% C4MR. The resists were dissolved in propylene glycol methyl ether acetate and the solutions were filtered through 0.2 μm polytetrafluoroethylene filters. The solutions were spin-coated to form films that received a postapply bake of 90 °C for 2 min to produce 50 nm thick films. After exposure, no PEB was used and the films were directly developed in 0.26*N* tetramethylammonium hydroxide for 30 s and rinsed with de-ionized water.

B. Synthesis

1. NBnHPF

9,9-bis(4-hydroxyphenyl) fluorene (3.00 g, 8.56 mmol, 1 equiv) was dissolved in acetone along with 2-nitrobenzyl bromide (1.94 g, 8.99 mmol, 1.05 equiv) and 18-crown-6 (113 mg, 0.43 mmol, 0.05 equiv). Potassium carbonate (1.30 g, 9.42 mmol, 1.1 equiv) was added and the mixture was stirred under reflux overnight. The reaction mixture was poured onto water and extracted with dichloromethane. The organic layer was washed twice with water and dried over $MgSO_4$, and the solvent was removed using a rotary evaporator to yield a pale yellow oil. The oil was purified by flash chromatography using dichloromethane. The first product off the column was the disubstituted product (rf=0.74) and the second product was the desired monosubstituted NBnHPF (rf=0.31). After evaporating the solvent, 9-(4-(2-nitrobenzyloxy)phenyl)-9-(4-hydroxyphenyl) fluorene was obtained as a pure white solid (1.53 g, 37% yield). ^{1}H-NMR (300 MHz, $CDCl_3$) δ (ppm) 8.14 (d, 1H), 7.86 (d, 1H), 7.75 (d, 2H), 7.66 (t, 1H), 7.46 (t, 1H), 7.37 (d, 2H), 7.35 (t, 2H), 7.26 (t, 2H), 7.14 (d, 2H), 7.06 (d, 2H), 6.83 (d, 2H), 6.70 (d, 2H), 5.43 (s, 2H).

2. NBnDCh

Deoxycholic acid (2.00 g, 5.09 mmol, 1.16 equiv) and 2-nitrobenzyl bromide (0.95 g, 4.84 mmol, 1 equiv) were dissolved in 15–20 ml of benzene to give a cloudy solution. 1,8-diazabicyclo[5.4.0]undec-7-ene (0.853 g, 5.60 mmol, 1.27 equiv) was dripped into the solution and a precipitate begins to appear, which dissolves over time with heating to give a clear solution. The reaction mixture is heated to 80 °C overnight with stirring. Upon cooling, a white precipitate appears, and ethyl acetate and water are added to the solution. The organic layer is separated and washed with water. The solvent is removed using a rotary evaporator. Recrystallization using ethanol gives 2-nitrobenzyl deoxycholate as a white solid (1.20 g, 52% yield). ^{1}H-NMR (300 MHz, DMSO) δ (ppm) 8.10 (d, 1H), 7.77 (t, 1H), 7.62 (m, 2H), 5.38 (s, 2H), 4.52 (d, 1H), 4.19 (d, 1H), 3.75 (s, 1H), 2.45–2.21 (m, 2H), 1.83–0.94 (m, 25H), 0.90 (d, 3H), 0.82 (s, 3H), 0.55 (s, 3H).

III. RESULTS AND DISCUSSION

While NBnHPF and NBnDCh could certainly be used only as pure single component resists, their sensitivity would likely be much higher than could be achieved by blending them into other soluble compounds, such as the C4MR used here, which reduces the total conversion of photosensitive protecting group in the mixture that is required to reach a bulk soluble state. In dissolution inhibitor (DI) based polymer systems such as DNQ/novolak, an inhibitor loading of 15%–30% is sufficient to provide the dissolution contrast needed to pattern the resist.[23] Using molecular resists in a

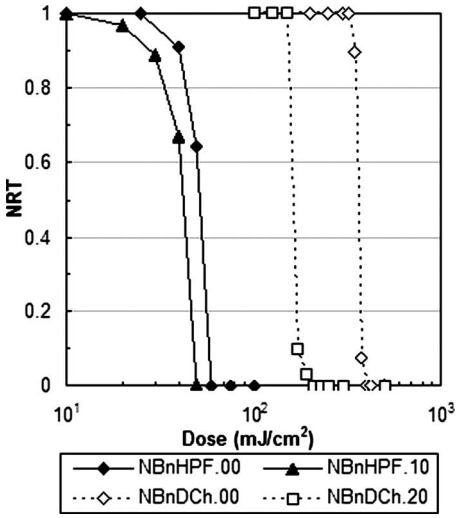

FIG. 2. DUV (248 nm) contrast curves for NBnHPF.00, NBnHPF.10, NBnDCh.00, and NBnDCh.20.

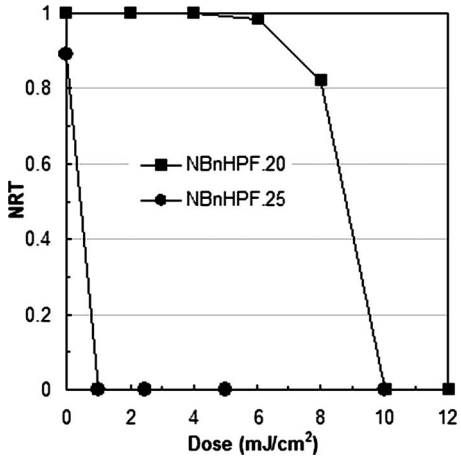

FIG. 3. DUV (248 nm) contrast curves for NBnHPF.20 and NBnHPF.25.

sub-100-nm thick film, this is an insufficient inhibitor loading and the entire film would dissolve over typical development times. Rather, DI loadings of greater than 70%–80% are required to make the entire film insoluble in some cases. Since the DI is now the primary resist component, it is easier to discuss different formulations based on the amount of dissolution promoter (DP), or base soluble molecular resist, added to the photosensitive insoluble compounds. While the soluble unprotected compounds, i.e., 9,9-bis(4-hydroxyphenyl)fluorene and deoxycholic acid, could certainly be added to serve this purpose, C4MR was added as the DP in this initial study because of its relatively compact size and large number of OH groups. The large numbers of OH groups should create a strong hydrogen bonding between the soluble C4MR and the insoluble components, and it was felt that this could act to improve contrast by reducing the leaching of C4MR from the unexposed and partially exposed regions of the resist during development. Four different blends of NBnHPF and C4MR were patterned with 0, 10, 20, and 25 wt % C4MR. While higher loadings of C4MR were attempted, they all showed significant dark loss that was too large to be used for patterning sub-100-nm thick films. Four different blends of NBnDCh and C4MR were made with 0, 20, 40, and 50 wt % C4MR. The blends with 40 and 50 wt % C4MR (NBnDCh.40 and NBnDCh.50) again showed too much dark loss and/or delamination to be successfully patterned. All resist formulations were patterned on hexamethyldisilazane primed silicon or silicon nitride substrates, since on unprimed substrates, these compounds all exhibited adhesion and delamination problems during developing.

Four of the resist formulations showed DUV (248 nm) sensitivity that was worse than typical CAR sensitivity. The DUV contrast curves for NBnHPF.00, NBnHPF.10, NBnDCh.00, and NBnDCh.20 are shown in Fig. 2. While the resists based on NBnHPF showed much better sensitivity than the NBnDCh resists, the NBnDCh resists showed better contrast than the NBnHPF resists. As expected, the sensitivity is improved substantially in both systems when more dissolution promoter is added. NBnHPF.00 had a dose-to-clear (E_0) of 60 mJ/cm^2 and a contrast ratio of 7.6, while NBnHPF.10 had a E_0 of 50 mJ/cm^2 and a contrast of 6.5. While these sensitivity values are slightly higher than most typical CARs, they are significantly lower than those reported for most non-CARs such as DNQ-novolak. The contrast is just marginally lower than top performing CARs and is competitive with some CARs used in industrial manufacturing. The deoxycholate based systems show sensitivity that is similar to or slightly worse than other dissolution inhibitor based non-CARs, but have much better contrast.[23] The E_0 and contrast for NBnDCh.00 were 377 mJ/cm^2 and 27.3, respectively, and NBnDCh.20 had an E_0 of 172 mJ/cm^2 and a contrast of 16.7.

Interestingly, two of the non-CAR molecular resist formulations characterized here perform equivalent to or even superior to CARs. For comparison to a previous study in our laboratory,[24] a molecular resist CAR based on a tBoc protected tris(4-hydroxyphenyl)ethane, imaged using 5 mol % triphenylsulfonium nonaflate as a photoacid generator (PAG), had a sensitivity of 8 mJ/cm^2 with a contrast of 6.4 under DUV exposures. The DUV contrast curves for NBnHPF.20 and NBnHPF.25 are shown in Fig. 3. The sensitivity for NBnHPF.20 was 10 mJ/cm^2 with a contrast of 8.3. NBnHPF.25 has a dose-to-clear of only 1 mJ/cm^2 with a minor dark loss of around 5 nm film thickness. To our knowledge, this is the best sensitivity ever reported for a nonchemically amplified resist and would be considered a very sensitive resist even if it were a CAR. These two resists really show the possibilities of this resist design scheme, i.e., that nonchemically amplified resists can be made, which perform equivalent to or possibly superior to CARs. The sensitivity can be highly tuned simply by changing the dissolution promoter loading.

In an effort to study and quantify the differences between the NBnHPF and NBnDCh systems, FTIR studies of the photochemical conversion rates of the nitrobenzyl (NBn) group were performed for each system. The decrease in the

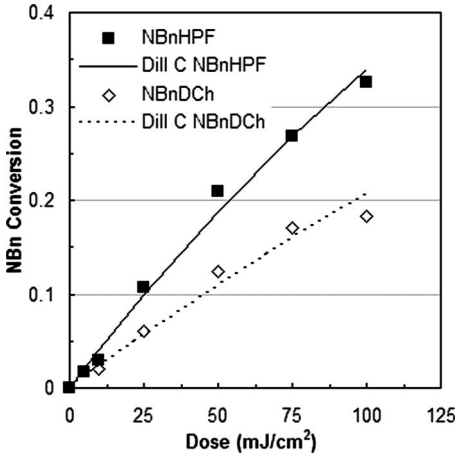

FIG. 4. Conversion of NBn groups for NBnHPF.20 and NBnDCh.00, and a fit of the data using a Dill C model.

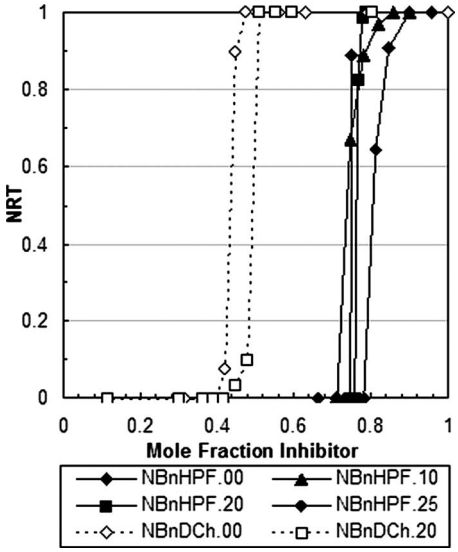

FIG. 5. Inhibitor loading at the point of solubility transition for the different formulations of NBnHPF and NBnDCh.

nitroabsorbance peak at 1525 cm^{-1} was used to monitor the photolysis of the protecting group. The data were fitted using a Dill C model as shown in Eq. (1).[25] The experimental data and the Dill C model fit to the data are shown in Fig. 4. The Dill C value for NBnHPF.20 was 0.0042 cm^2/mJ, and the Dill C value for NBnDCh.00 was 0.0023 cm^2/mJ. These values are consistent with other studies of the photochemical rate constant for nitrobenzyl groups. For example, a Dill C value of 0.0094 cm^2/mJ was previously reported for a nitrobenzyl tosylate photoacid generator in a polystyrene matrix[26] and a Dill C value of 0.00243 cm^2/mJ was recently reported for a nitrobenzyl N,N-diisopropyl carbamate photobase generator in poly(methyl methacrylate).[27] As expected, the Dill C value for this nonionic moiety is lower than triarylsulfonium PAGs, which typically have Dill C values in the range of 0.025–0.05 cm^2/mJ,[28]

$$[ROH] = [RONBn]_0(1 - e^{-CE}). \quad (1)$$

Although the Dill C for the NBnDCh systems is about half that of the NBnHPF systems, the dose-to-clear for the NBnDCh formulations is 5–20 times higher than similar NBnHPF formulations. To better understand the differences between the two systems, the contrast curves and the Dill C parameters were combined to examine the inhibitor loading at the point of solubility-switching in these C4MR mixture based resists. Figure 5 shows the normalized remaining thickness versus mole fraction of inhibitor remaining in the film. As expected, the six contrast curves collapse onto two different groups, one group for the NBnDCh resists that undergo a solubility switch at about 0.45 mol fraction protected inhibitor, and a second group for the NBnHPF resists with all the different formulations clearing at approximately 0.75 mol fraction protected inhibitor. The worse sensitivity of the NBnDCh based resists is because they both have a lower Dill C value and require much higher conversion of the protected NBnDCh inhibitor than in the case of the NBnHPF based resists. NBnDCh has such a different inhibitor loading at the solubility threshold compared with NBnHPF, most likely because of the different base soluble groups in each system. NBnHPF has phenolic groups that deprotonate during development, while NBnDCh has carboxylic acid groups. Although the exact reasons why the two different solubilizing groups might show this kind of difference are currently unknown, it has been previously shown that carboxylic acid and phenol based resists can show quite different dissolution behaviors.[29] Since carboxylic acid based systems show a greater propensity for swelling than phenol based systems, it is possible that some small levels of swelling in the NBnDCh system is the source of the difference between the two systems, but further studies are required.

Figure 5 also reveals the key to the high sensitivity and good contrast of this design scheme. The materials show a sharp thickness response to small changes in the conversion of the protected inhibitor, and if the ratio of protected inhibitor to C4MR dissolution promoter is chosen properly, then a very low photochemical conversion of the inhibitor is required to reach a soluble state. In other words, by increasing the dissolution promoter loading, the conversion required to reach the solubility threshold is reduced. NBnHPF.20 requires only about 5% conversion of the nitrobenzyl ether protecting groups to become soluble, while NBnHPF.25 requires less than 0.5% conversion to cross the solubility threshold. Although the photoreaction rate constants for these nonionic systems are lower than the conventional ionic photoacid generators used in typical CARs, the very low conversion required in the non-CARs allows them to maintain good to excellent sensitivity. Additionally, no scumming is detectible by ellipsometry in patterned films even though 75% of the film is composed of nominally base insoluble molecules. This is a property that is likely unique to molecular resists compared to polymeric based inhibitor systems.

In most typical resist systems, if a resist has good sensitivity in DUV optical patterning, it will have reasonably good sensitivity in higher energy patterning processes such as e-beam or EUV despite the change in the exposure mecha-

nism. This is the reason why most current EUV resists are based on CAR platforms that were originally used for KrF patterning such as tert-butyl methacrylate/hydroxystyene copolymers (ESCAP-lik3-resists),[30] and thus, it is generally accepted that entirely new resist design platforms do not have to be developed for the move to EUV such as was the case with the move to ArF patterning from KrF patterning[31] or when movement to F_2 excimer laser based patterning was considered.[32] For this reason, it was expected that the resist materials explored in this work would still show reasonable sensitivity under e-beam patterning. However, when high resolution patterning of NBnHPF.20 was attempted using 100 keV e-beam, no patterning was observed even at doses as high as 3000 $\mu C/cm^2$. Only a slight thickness modulation was observed in areas that should nominally be patterned and was the only obvious evidence that the sample had been exposed at all. When NBnDCh was patterned using e-beam lithography, no thickness modulation after development could be observed at all. Likewise, large area contrast curves of NBnHPF.20 patterned using EUV did not clear even up to doses of 70 mJ/cm^2.

A previous study[26] using 2-nitrobenzyl tosylate PAGs loaded at 5 wt % in a polystyrene matrix showed that the nitrobenzyl groups are active under 100 keV e-beam exposure, so the nitrobenzyl groups should undergo conversion. If NBnHPF.20 had the same Dill C value under 100 keV e-beam as reported for 2-nitrobenzyl tosylate[26] (0.005 $cm^2/\mu C$), it would have patterned at approximately 10–15 $\mu C/cm^2$ based on the data in Fig. 5. While there are obvious differences in the bulk matrix and the nitrobenzyl group attachment, the most important difference between the two different studies is the relative loading of the nitrobenzyl group. Considering only the nitrobenzyl group ($C_7H_6NO_2$) relative to all other solids, NBnHPF.20 has tenfold higher loading by mass of the nitrobenzyl group than the PAG study. Under DUV, the resist still behaves as expected when significantly increasing the loading of a photoactive compound. Under high energy exposures, the resist behavior changes drastically when the active compound loading is significantly increased. This is likely due to the change in exposure mechanism going from DUV, where the patterning is primarily by direct photon absorption, to EUV and e-beam, where the patterning occurs by a more complicated series of excited state electron transfers.[33] The exact cause of the loss of sensitivity is unknown, but is likely due to some additional mechanism such as cross-linking that arises or becomes more important under high energy exposures when the active species concentration is increased. Further study is needed to understand the cause of this sensitivity loss and what effect it might have on future non-CA resists for e-beam and EUV. Likewise, this could also have a strong effect on CARs that have higher loadings of photoactive species such as PAGs.

Although a significant loss of sensitivity makes this specific set of compounds unsuitable for use in EUV and e-beam, it is possible that using a different active species besides the 2-nitrobenzyl group could show improvements that would allow the use of this design scheme with those exposure methods. Despite the problems under high energy exposures, several of the current compounds show excellent sensitivity and contrast under DUV exposures. High resolution patterning of these compounds under 248 and 193 nm should likewise show good performance. These studies are underway.

IV. CONCLUSIONS

Two new nonchemically amplified molecular resists have been synthesized and characterized. The sensitivity and contrast could be tuned by changing the amount of dissolution promoter blended into the resist formulations. NBnDCh, a molecular resist based on 2-nitrobenzyl ester protected deoxycholic acid, showed an excellent contrast ratio of 27.3 and a DUV sensitivity of 377 mJ/cm^2. Blending 10 wt % of a dissolution promoter improved the sensitivity to 172 mJ/cm^2. NBnHPF, a resist based on a 9,9-bis(4-hydroxyphenyl)fluorene molecular resist core that was protected with a single nitrobenzyl ether, showed DUV sensitivity of 60 mJ/cm^2 and a contrast ratio of 7.6. Blending 20 wt % of a calixarene dissolution promoter improved its sensitivity and contrast to 10 and 8.3 mJ/cm^2, respectively. Addition of 25 wt % of the dissolution promoter to NBnHPF improved sensitivity down to 1 mJ/cm^2. The superior sensitivity of the NBnHPF systems relative to the NBnDCh systems was due to the fact that they had not only a higher Dill C parameter, but also required much less conversion to cross the solubility threshold. NBnHPF systems undergo a solubility transition at around 75 mol % inhibitor while the solubility transition for NBnDCh systems is around 45 mol % inhibitor, meaning that an equivalent formulation of NBnDCh would require at least 200% of the conversion that a NBnHPF formulation would require. The excellent sensitivity in NBnHPF systems is explained by the high levels of inhibitor at the solubility threshold. NBnHPF.20 clears with only 5% conversion of the photosensitive protecting group, while NBnHPF.25 only requires 0.5% conversion to clear. Despite the high sensitivity under DUV, these resists would not pattern under EUV and e-beam, even up to doses as high as 3000 $\mu C/cm^2$ (100 keV). The cause of complete loss of sensitivity of the systems under high energy exposures is unknown, but is likely related to the change in the patterning mechanism under ionizing radiation.

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