Weak intermolecular hydrogen bonding is an important factor for NA in ALPO-5 and may cause the self-assembly of molecular aggregates or chains that are aligned by the host channels. Similar aggregates may form in the other hosts. Structural work is in progress to further elucidate the alignment mechanism in these materials.

Three modes of SHG tuning are demonstrated by these materials: (1) variation in loading level, (2) variation in guest structure or composition, and (3) variation in host framework charge or dielectric constant. This allows great flexibility in formulating promising new combinations and shows that there are many avenues left to be explored. The systems are particularly important in providing the foundation for understanding the self-assembly of molecules and both inter- and intramolecular cluster interactions in supramolecular lattices. Molecular modeling studies of these properties are in progress.

Acknowledgment. The research support of the Office of Naval Research and E. I. Du Pont is gratefully acknowledged. We also thank Seth Marder, Albert Steagman, and Joe Perry of Jet Propulsion Laboratory for their advice and assistance in SHG measurements at 1.907 μm.

Supplementary Material Available: Diffuse reflectance UV–vis spectra of pure NA, pure DMNA, and pure NPNO at various concentrations in the various described molecular sieves (3 pages). Ordering information is given on any current masthead page.

Characterization of a Novolac-Based Three-Component Deep-UV Resist

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Received July 16, 1990

High-sensitivity positive-tone deep-UV resists are described that utilize acid-catalyzed chemistry in novolac resin. These resists are composed of an acid-sensitive dissolution inhibitor, an acid photogenerator, and novolac resin. The lithographic functioning and processing of these resists are very similar to the familiar diazonaphthoquinone/novolac systems but with nearly a 100-fold increase in sensitivity. The resist sensitivity shows a surprising dependency on the choice of casting solvent, and this effect has been demonstrated to be related to the resist chemistry, which has been studied by using ^2H NMR spectroscopy. The resist mechanism has been demonstrated to be primarily due to acid catalyzed thermolysis of the *tert*-butyl carbonate functional groups. The imaging characteristics of these resists is limited by the absorbance of the novolac resin, but submicron $[TTPFe^{IV}(C_6H_4CH_3\text{-}p)]^+$ has been obtained.

Introduction

Lithographic technology has advanced to the point that resolution capability well below 1 μm is now practiced in full-scale manufacturing of semiconductor devices. This may be achieved by use of high numerical aperture *i*-line or *g*-line step-and-repeat tools or by use of deep-UV lithography (200–300 nm). In the diffraction limit, the use of shorter wavelength radiation offers improved resolution and this has been demonstrated experimentally.[1,2] It now appears that use of deep-UV lithography may allow optical lithography to be extended well below 0.5-μm resolution. Deep-UV lithography has now been demonstrated by using commercial deep-UV lithographic tools that have both relatively broadband mercury emission sources and very narrow 248-nm excimer laser light sources. However, this has necessitated the development of new deep-UV resist materials since the traditional diazonaphthoquinone/novolac resists are inadequate for deep-UV lithography.[3,4]

Resist development for deep-UV lithography has evolved along several paths since the initial work with poly(methyl methacrylate) (PMMA).[1] PMMA resist functions by photoinduced cleavage of the polymer main chain that renders the exposed region of the polymer more soluble in certain developer solvents. Several other acrylate-type polymers are also sensitive in the deep-UV region as are isopropenyl ketone polymers.[5] In addition, negative deep-UV systems have been developed on the basis of the use of azide sensitizers that cross-link upon exposure to deep-UV radiation.[6]

All of these approaches however suffer from lack of sufficient sensitivity to deep-UV radiation. The exposure doses required to achieve reasonable throughput are considerably less for deep-UV lithography than for longer wavelengths. This appears to be true both for conventional mercury light sources and for excimer laser light sources. The higher sensitivity demand for deep-UV resists required the development of resists that were not limited by the quantum yield for the photochemical conversion.

High-sensitivity resists for deep-UV application have been developed around the concept known as chemical amplification, which separates the photochemical event from the bulk chemical change that is ultimately responsible for imaging.[7] This has been accomplished by ex-

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ploiting photogenerating acid sources that, after irradiation, can affect chemical conversions with catalytic chain lengths as large as 1000.[8] This principle has been used to develop resists based on a wide variety of catalyzed processes including polymerizations, depolymerizations, cross-linking reactions, and functional group changes which bring about changes in the polarity of the polymers.

Conceptually the resists based on photogeneration of catalysts would appear to be distinctly different from the diazonaphthoquinone/novolac resists, which are the current cornerstone of the resist industry. However, by use of dissolution inhibition three-component resist design, the advantages of both systems can be combined into a single system. Thus both chemical amplification and dissolution inhibition mechanisms are effectively incorporated in a single-resist system. Three-component resist systems based on dissolution inhibition contain an aqueous base developable resin, an acid photogenerator, and an acid-labile dissolution inhibitor. After exposure and postbake, the dissolution inhibitor is destroyed, which allows for discriminatory development rates between exposed and unexposed photoresist film.[9-13] In this paper we describe the functioning of one such system and point out the advantages gained from this approach as well as the limitation imposed by the use of novolac.

Experimental Section

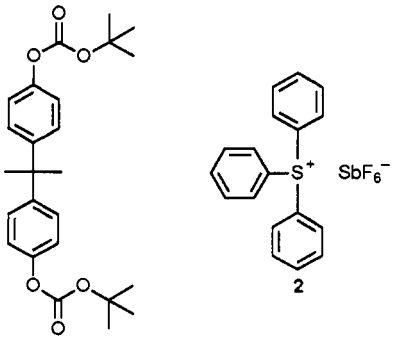
Materials. 2,2-Bis(4-[(*tert*-butoxycarbonyl)oxy]phenyl)-propane (1), 2,2-bis(4-[(*tert*-butoxycarbonyl)oxy]-2,3,5,6-tetradeuteriophenyl)propane (4), and 4,4'-bis[(*tert*-butoxycarbonyl) oxy]phenyl sulfone (7) were prepared by reaction of the corresponding phenols with di-*tert*-butyl dicarbonate in the presence of potassium carbonate and 18-crown-6.[14] 2,2-Bis(4-[(methoxycarbonyl)oxy]phenyl)propane (6) was prepared by reaction of 2,2-bis(4-hydroxyphenyl)propane with methyl chloroformate in the presence of pyridine. Triphenylsulfonium hexafluoroantimonate was prepared by a published procedure.[15] Novolac resin formulated in bis(2-methoxyethyl) ether (diglyme) and 2-methoxyethyl acetate (ethyl cellosolve acetate or ECA) was obtained from Reichold Chemical Co. under the trade name of Varcum. The novolac/ECA solutions also contain small amounts (<10%) of *n*-butyl acetate as well as xylene.

Measurements. Ultraviolet absorption spectra were recorded on a Hewlett-Packard Model 8450A UV–visible spectrometer, IR spectra on an IBM FTIR Model 44, and ^2H NMR spectra on an AM500 NMR spectrometer at 76 MHz, operating in an unlocked mode at 298 K. ^2H chemical shifts were referenced to residual acetone[$^2H_1$] at δ 2.04. Exposure doses were measured with an Optical Associates Model 355 exposure monitor equipped with 254-nm sensitive probes. Film thicknesses were measured on a Tencor Alpha Step 200. Scanning electron microscopy was performed on a Philips 505 SEM.

Resist Processing. Nominal 1-μm-thick films were prepared on silicon substrates by spin coating of resist solutions which were filtered through 0.2-μm filters. The substrates were then baked at 90 °C for 5 min on a hot plate. The optical exposure was then done followed by a subsequent bake on a hot plate. Contact exposures were done on an Optical Associates 30/5exposure tool through 254-nm bandpass filters. Broadband deep-UV scanning projection printing was done with a Perkin-Elmer 500 Micralign exposure system with a UV-2 filter that transmits light between 220 and 290 nm. Excimer laser exposures were performed at 248 nm with a GCA excimer laser based 10X system with 0.35 NA. Resist development was done by immersion in a rapidly stirred developer solution.

Results and Discussion

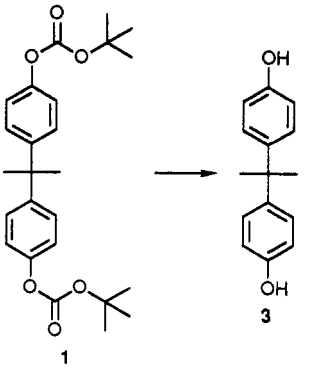
Resist Performance. The resist is composed of an acid-sensitive dissolution inhibitor, an acid photogenerator, and novolac. The initial studies used the dicarbonate derivative 1 as the dissolution inhibitor and sulfonium salt



1 2

2 as the acid photogenerator. This resist formulation is referred to as BPABOC. Carbonate 1 is quite effective as a dissolution inhibitor when loaded in 15–20 wt % versus novolac. A typical BPABOC composition consists of 16% of 1, 4% of sulfonium salt 2, and 80% novolac by weight.

The *tert*-butyl carbonate 1 is thermally labile and when heated in the presence of acid decomposes to give bisphenol A (3, eq 1) at temperatures below 100 °C. The



1 3 (1)

phenol 3 has little if any dissolution inhibition properties, and thus in resist films where decomposition of 1 has occurred, aqueous base development is quite rapid relative to the unexposed film.

BPABOC resist is quite sensitive to deep-UV radiation and functions in a positive mode for deep-UV lithography. Typical dose requirements are 5–15 mJ/cm^2 at 254 nm. The exposure is followed by a subsequent bake and then development with aqueous base developer. While the process parameters for this resist were not completely optimized, the best results were obtained for a 90 °C bake temperature and development with dilute aqueous potassium hydroxide (0.18 N) developer. A study of the effect of bake temperature on the dissolution rate was carried out by quartz crystal microbalance measurement.[16] Figure 1 shows the development curves for 1-μm-thick BPABOC resist films exposed to a dose of 6.0 mJ/cm^2 at 254 nm. The thermolysis was performed at various tem-

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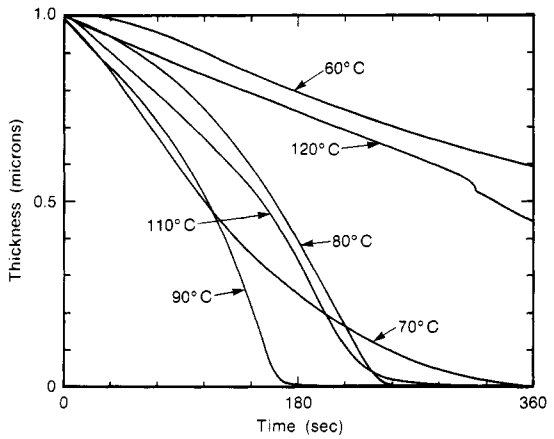


Figure 1. Effect of postexposure bake temperature on resist performance.

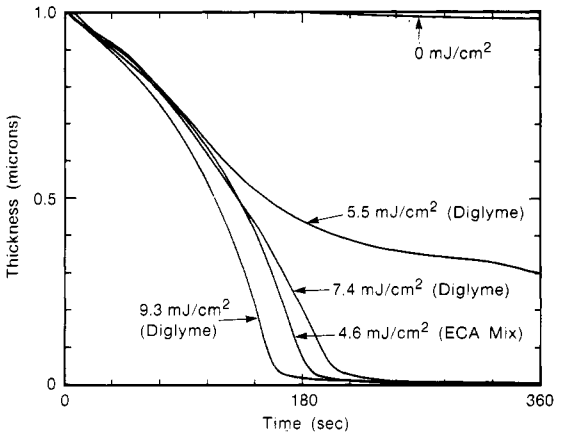


Figure 2. Effect of casting solvent on resist performance.

peratures for 90 s followed by development with 0.18 N potassium hydroxide solution. The fastest rate was observed when the thermolysis was carried out at 90 °C. The development rates at temperatures below 90 °C probably decrease due to incomplete carbonate removal (eq I) whereas decreasing rates at thermolysis temperature above 90 °C are likely due to acid-catalyzed cross-linking of novolac.

The dose requirement for BPABOC is dependent to some degree on the choice of casting solvent. The novolac resin used for these studies is available in either diglyme or ethyl cellosolve acetate (ECA) solution. When formulated in diglyme, the resist has less sensitivity to irradiation with deep-UV light than when formulated in ECA. Figure 2 shows quartz crystal microbalance analysis of the development rate for both solvent systems at various doses. Unexposed film development is shown at the top of the figure. In addition development curves are shown for three different exposure doses of resist formulated in diglyme. The films were exposed at 254 nm, heated at 90 °C for 90 s, and then developed with 0.18 N KOH solution. At the 5.5 mJ/cm^2 exposure dose, approximately 0.3 μm of film remained after development. At 7.4 and 9.3 mJ/cm^2 complete film development occurred within the 6-min development time. The development rate for BPABOC formulated in ECA mix was carried out with 4.6 mJ/cm^2 followed by the standard process. It is evident that the 4.6 mJ/cm^2 dose for the film spun from ECA is roughly equivalent to an 8 mJ/cm^2 exposure for the same resist formulated in diglyme. Thus a nearly 2-fold increase in sensitivity for the resist can be achieved merely by varying the casting solvent.

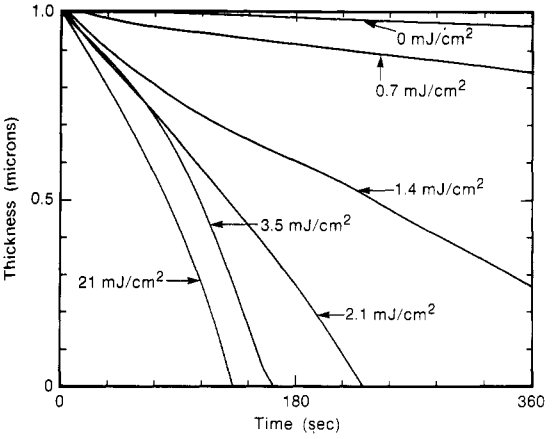


Figure 3. Development curves for low-exposure doses of resist formulated in ECA solvent mix.

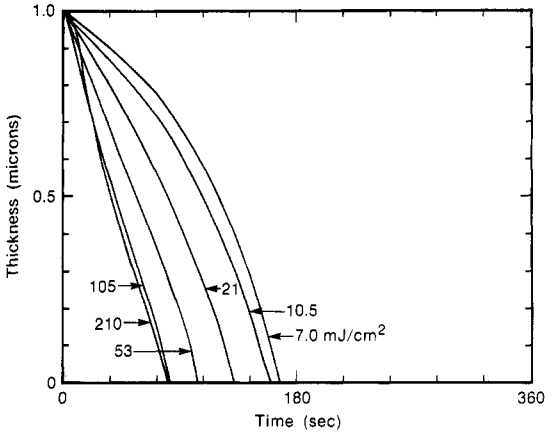


Figure 4. Development curves for high-exposure doses of resist formulated in ECA solvent mix.

Quartz crystal microbalance studies were carried out for BPABOC formulated in ECA (Figure 3) after exposure to various doses of 254-nm radiation, thermolysis at 90 °C, and development with 0.18 N KOH solution. The results show that resist performance is adequate at doses greater than 3.5 mJ/cm^2. At lower doses imaging cannot be accomplished under these processing conditions without appreciable film loss in the unexposed regions. For resist films exposed at doses higher than 3.5 mJ/cm^2 the dissolution rate increases only slightly. For example, a 6-fold increase in dose from 3.5 to 21 mJ/cm^2 produces only about a 20% increase in dissolution rate. The resist shows no evidence of appreciable cross-linking even at very high doses provided that the bake temperature is maintained at 90 °C. There is no decrease in development rate even at doses as high as 200 mJ/cm^2 (Figure 4). The contrast for the resist can be obtained from this data. The contrast was measured for the lowest lithographically useful dose of 3.5 mJ/cm^2 (Figure 5) and is about 1.8.

Resist Mechanism. While the expected resist chemistry is that shown in eq 1, it was decided that the mechanism should be examined in detail due to the changes in photospeed that were observed on change of casting solvent. Initial experiments were performed by studying the change in carbonyl absorbance in the IR, which is the traditional method used to study *t*-BOC chemistry.[17] These studies were carried out by spin 7 films on 1-mm-thick NaCl plates. Exposures were performed followed by

(17) Ito, H.; Willson, C. G. In *Polymers in Electronics*; Davidson, T., Ed.; American Chemical Society: Washington D.C., 1983; p 3.

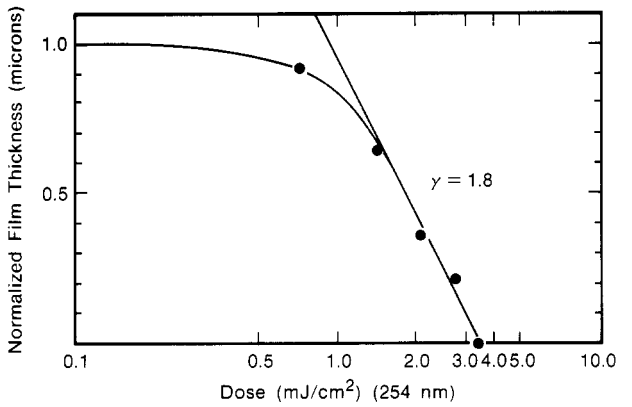
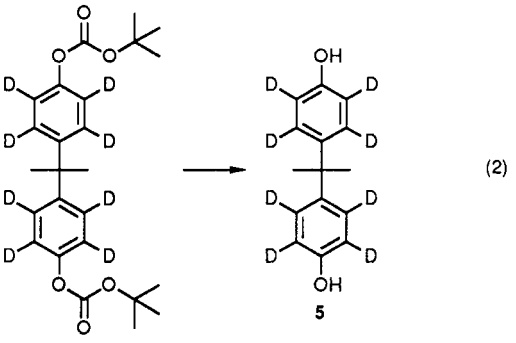


Figure 5. Contrast curve for resist formulated $TTPFe^{III}(C_6H_5)$ ECA solvent mix.

thermolysis at 90 °C. Infrared spectra were taken before and after exposure. Remarkably, when the films cast from diglyme were exposed at 3.5 mJ/cm² and then heated, very little change occurred in the carbonyl absorbance (Figure 6). While this dose is not lithographically useful (see Figure 1), some loss of carbonate functionality would be expected at this dose. The same studies were carried out for films cast from ECA. When exposed to 3.5 mJ/cm² and heated at 90 °C, these films showed extensive carbonyl loss. At higher doses (20 mJ/cm²) complete loss of the carbonyl group was observed for resist films cast from ECA. The infrared studies are consistent with the loss of photospeed associated with use of diglyme solvent.

More insight into the mechanism was obtained by ^2H nuclear magnetic resonance (NMR) studies of the resist films. Dicarbonate **4** was prepared containing greater than 99% ^2H incorporation at all positions on the aromatic rings (eq 2). The deuterium-labeled dicarbonate was then used



4 5 (2)

for resist formulations. Films were spin cast, exposed to 5 mJ/cm² of 254-nm light, and heated at 90 °C. The processed resist films were analyzed in acetone solution by ^2H NMR. Spectra of pure **4** and **5** were measured to confirm the expected upfield shift of the aromatic deuterons on conversion of the dicarbonate **4** to phenolic derivative **5**.[18] Resist film cast from ECA showed complete conversion of dicarbonate to phenol with a 5 mJ/cm² exposure dose (Figure 7). However, the ^2H NMR spectrum of film cast from diglyme shows only approximately 73% conversion to phenol (downfield region shown in Figure 8) at the same dose. These results explain the observed difference in sensitivity between the two solvent systems. The reasons for the lower conversion in diglyme is unexpected and may be due to basic impurities which limit the

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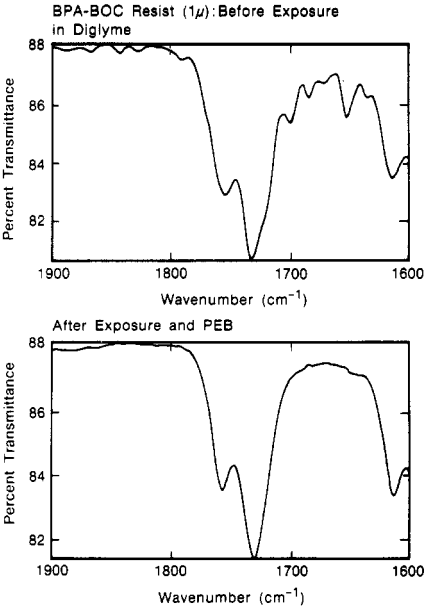


Figure 6. Infrared spectra of at 25 °C of film before exposure and after exposure and post exposure bake.

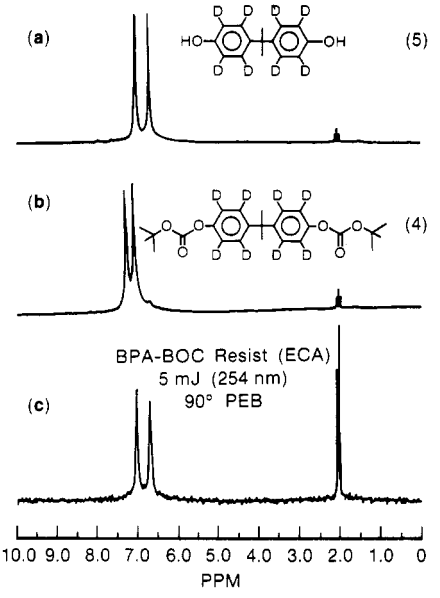


Figure 7. ^2H NMR spectra of (a) deuterated bisphenol A **5**, (b) deuterated dicarbonate derivative **4**, and (c) BPABOC resist film formulated from ECA solvent mix exposed and postbaked.

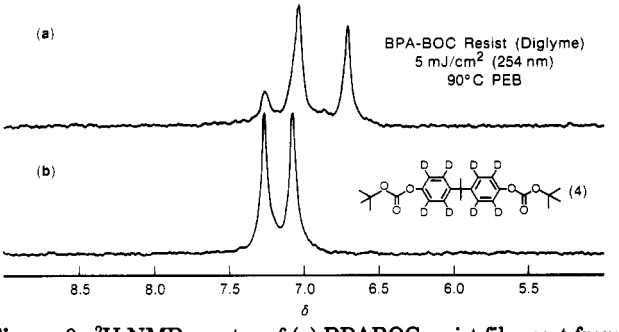
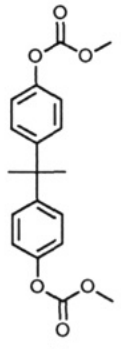


Figure 8. ^2H NMR spectra of (a) BPABOC resist film cast from diglyme, exposed, and postbaked, and (b) dicarbonate **4**. For the exposed resist film (a) one residual dicarbonate resonance is observed at δ 7.25 and a bisphenol A resonance at δ 6.70. Resolution enhancement reveals the resonance at δ 7.0 to be a composite of the second residual dicarbonate resonance at δ 7.07 and a bisphenol A resonance at δ 7.03 (see Figure 7).

catalytic chain length for the *tert*-butyl carbonate removal.

^{2}H NMR studies were also useful in studying the storage stability of the resist reactions A resist formulation was prepared in ECA by using the deuterated dicarbonate **4** and stored at room temperature for 6 months and periodically analyzed by ^{2}H NMR. The results showed that the carbonate is completely stable in the resist formulation. No observable phenol (**5**) formation was observed. This stability was corroborated by functional testing involving quartz crystal microbalance experiments that showed no appreciable change in development rate for resist samples aged for 6 months.

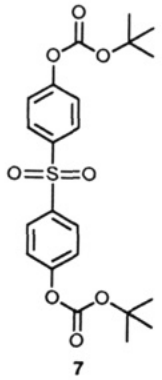
While acid-catalyzed thermolysis of the dissolution inhibitor **1** probably accounts for the bulk of the activity of this resist system, it is not possible to preclude a dissolution inhibition contribution from the sulfonium salt **2** as this mechanism has been previously reported.[19] Such resists are generally considerably less sensitive than dissolution inhibition three-component systems. To evaluate this mechanistic possibility, a three-component system was prepared analogous to BPABOC but containing the acid-insensitive methyl carbonate **6** rather than **1**. Despite the



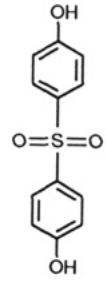
6

fact that **6** is essentially insensitive to acid-catalyzed thermolysis, positive relief images were obtained for the resist when processed in the same fashion as for the *tert*-butyl carbonate-containing resist (Figure 9). However the dose requirement was much larger (100 mJ/cm^2), and a stronger base strength developer was required. Resists formulated from **6** are likely to function merely due to the dissolution inhibition of the sulfonium salt. These results indicate that the contribution to dissolution inhibition from the salt **2** is very minor in the BPABOC system, which is operating at only 3–5% of the dose required to achieve useful rate differentiation from photolysis of the salt alone.

A variety of dissolution inhibitor molecules have been auditioned. One particularly interesting example is inhibitor **7**. There is reason to expect that this material



7



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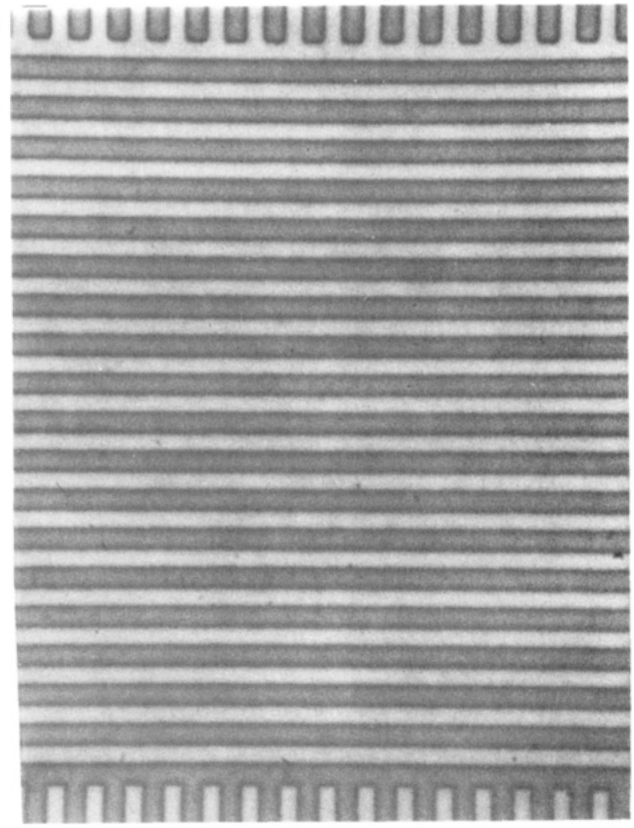

Figure 9. Optical micrographs of images from three-component resist containing dimethyl carbonate derivative **6**.

could provide better dissolution characteristics based on both the greater acidity of the product phenol (**8**) and the known ability of the sulfonyl substituent to manifest very efficient dissolution inhibition in novolac.[20] A resist formulation was prepared by using 16% of **7**, 4% **2**, and 80% novolac. Exposures were performed at 10 mJ/cm^2 followed by heating at 90 °C and development with aqueous base. While this resist did provide positive resist images, the contrast and overall resist performance were not as good as resist formulated with bisphenol A derived carbonate **1**. Surprisingly, the resist formulated with sulfone carbonate **7** showed low discriminatory rate behavior between the exposed and unexposed film. A variety of concentrations of sodium or potassium hydroxide solutions were screened initially but proved much too strong for this system even at very dilute concentrations. Better results were obtained from solutions prepared from tetramethylammonium hydroxide (TMAH). However even the best TMAH developer that was explored gave poor discriminatory rate behavior—only 6 times faster development rate for exposed versus unexposed film. Images could not be obtained without extensive film loss in the unexposed regions.

Novolac Absorbance. While the sensitivity of the BPABOC resist is very good for deep-UV application, the resolution is limited due to the unbleachable novolac absorbance in the deep-UV region. The UV spectrum for a 1.1-μm-thick film of BPABOC is shown in Figure 10. The absorbance per micrometer at 254 nm is 0.64, which corresponds to 23% transmission and does not change upon exposure. The effect of unbleachable absorbance is well-known to result in sloping wall profiles. This has been demonstrated experimentally in attempts to use diazo-

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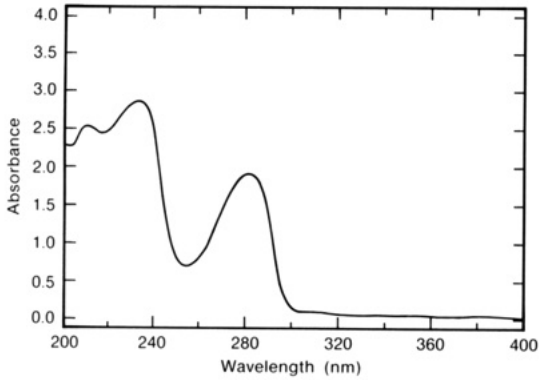

Figure 10. Ultraviolet absorption spectra of 1-μm film of BPABOC resist in novolac.

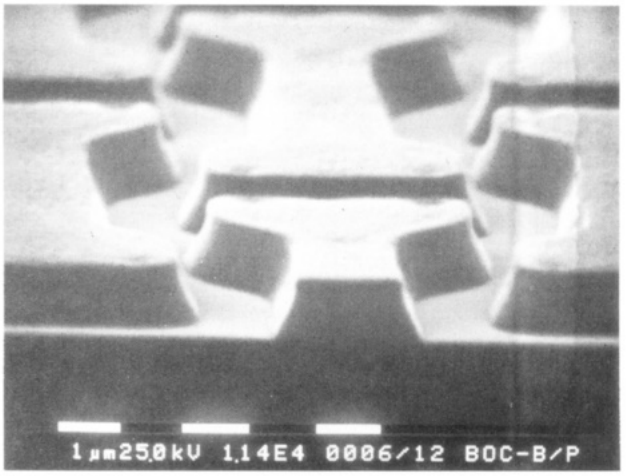

Figure 11. Scanning electron micrograph of images of obtained from scanning projection printing of BPABOC resist.

naphthoquinone/novolac resist for excimer laser deep-UV lithography at 248 nm.[21,22]

Exposures were performed on the three-component resist using a scanning projection exposure tool with light exposure between 220 and 290 nm. For this filter the resin absorbance issue is very important since this exposure bandwidth encompasses areas where resin absorbance is very intense. BPABOC resist films (1 μm thick) were exposed with a dose of about 7–10 mJ/cm^2. Resolution capability was possible for images down to 1 μm feature size. The scanning electron micrograph of images (Figure 11) show that the walls are nearly vertical near the top of the image but become sloping at the bottom half of the image. This undesirable shape is likely due to resin absorbance.

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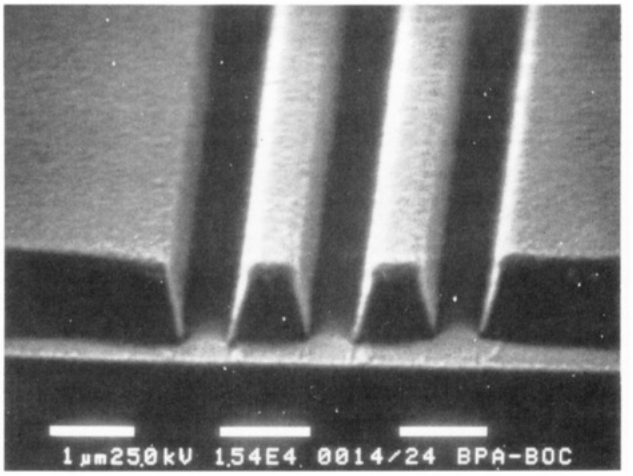

Figure 12. Scanning electron micrograph of 0.70-μm images from excimer laser stepper exposure of BPABOC resist.

The resist was also exposed on an excimer laser 10:1 reduction stepper (numerical aperature = 0.35). The excimer laser has output only at 248 nm, where the resin absorbance is at its minimum and thus the resin absorbance effect would be expected to be less severe than for the broadband scanning projection exposures. Films of 0.8-μm thickness were exposed at various doses and processed in the normal fashion. Best results were obtained at a dose of about 7–8 mJ/cm^2. At this dose, resolution could be achieved for images down to 0.65 μm. The features with 0.6-μm image size are extensively rounded at the top and eroded. The 0.70-μm features (Figure 12) appear similar to the 1.0-μm images obtained from scanning projection exposures. The top part of the image has a nearly vertical wall profile, but then sloping walls are observed for the bottom part of the image.

Conclusions

High-sensitivity positive-tone deep-UV resists have been developed that incorporate both dissolution inhibition and chemical amplification. These resists are composed of an acid-sensitive dissolution inhibitor, an acid photogenerator, and novolac resin. This study demonstrates the potential of three-component resist design to provide a deep-UV resist with processing characteristics very similar to the familiar diazonaphthoquinone/novolac systems but with nearly a 100-fold increase in sensitivity. The photogenerated differential dissolution rate arises from acid-catalyzed thermolysis of the *tert*-butyl carbonate groups on the inhibitor molecule. The practical application of the system studied is limited by the strong, unbleachable absorbance of the novolac matrix resin used in these formulations, but resolution of 0.7 μm has been demonstrated for projection printing at doses below 10 mJ/cm^2.

Registry No. **1**, 117458-06-7; **2**, 57840-38-7; **4**, 129104-69-4; **6**, 4824-74-2; **7**, 129104-70-7.