

Dissolution behavior of chemically amplified resist polymers for 248-, 193-, and 157-nm lithography

by H. Ito

The aqueous base development step is one of the most critical processes in modern lithographic imaging technology. Sinusoidal modulation of the exposing light intensity must be converted to a step function in the resist film during the development process. Thus, in designing high-performance resists, controlling the dissolution behavior of the resist polymer film in aqueous developer is of the utmost importance. This paper describes and compares the dissolution behavior of different polymers employed in chemically amplified imaging at 248, 193, and 157 nm. The polymers discussed in this paper are polyhydroxystyrene derivatives (248 nm), functionalized poly(cycloolefins) containing carboxylic acid (193 nm), and polymers bearing a hexafluoroisopropanol functionality for base solubility (157 nm).

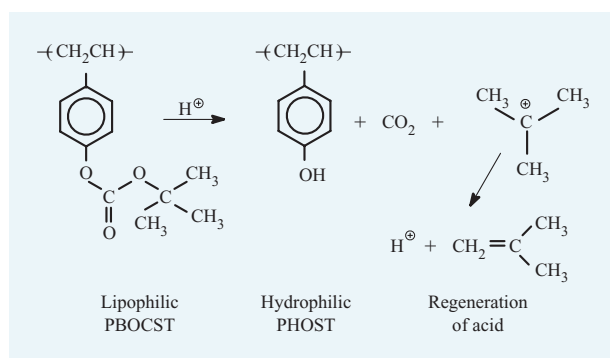
Introduction

Since the positive-tone novolac/diazoquinone resist replaced the rubber/azide negative resist in the microelectronics industry, the use of aqueous base as a developer has been mandated in the microlithographic fabrication technology. This stems not only from environmental consideration but also from the high resolution that aqueous base development can provide. The novolac/diazoquinone resist exposed at the G-line (436 nm) and I-line (365 nm) supported microelectronics device manufacturing for many years through relentless formulation improvement [1].

Because the resolution (R) is proportional to the exposing wavelength (λ) and inversely proportional to the numerical aperture (NA) of the lens ($R = k\lambda/NA$), higher resolutions are achieved by increasing the numerical aperture or by reducing the exposing wavelength. Reduction of the wavelength to the deep-UV region (~ 250 nm) became necessary to achieve higher resolution

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Scheme I

Acid-catalyzed deprotection for polarity change (tBOC resist); cleavage of a pendant group to convert a lipophilic polymer (PBOCST) to a hydrophilic polymer (PHOST).

in the 1980s. Because the above-mentioned G- and I-line resists consisting of a novolac resin and photoactive diazonaphthoquinone dissolution inhibitors do not perform adequately because of their excessive absorption in the deep-UV region, development of a revolutionary resist system was required. In addition, the imaging mechanism based on photochemical events that require several photons to generate one useful product did not provide high enough sensitivity to make deep-UV lithography using the novolac resist practical and economical.

Deep-UV lithography employing a KrF excimer laser (248 nm), which is the current workhorse producing devices with feature sizes smaller than 250 nm, depends on "chemical amplification" resist systems for required sensitivity [2]. The chemical amplification concept [3] derives its high sensitivity from photochemically induced acid-catalyzed reactions. Acid generated by photolysis undergoes a large number of chemical reactions without being consumed in one reaction. Positive-tone imaging by aqueous base development is achieved by acid-catalyzed deprotection of a lipophilic (base-insoluble) functionality to a hydrophilic (base-soluble) acidic group. The imaging mechanism is illustrated in **Scheme I**, where the IBM tBOC resist is shown as an example [4]. The high UV transparency at the exposing wavelength of 248 nm is achieved by selecting poly(4-hydroxystyrene) (PHOST) as the base polymer, which provides aqueous base developability and dry-etch resistance as well.

Resist systems for use in ArF (193-nm) excimer laser lithography are maturing rapidly [5]. Although the acid-catalyzed deprotection has remained as the imaging mechanism of choice, the polymer had to be changed from the aromatic to aliphatic structure for better transparency at 193 nm. Thus, the base-soluble functionality is primarily

carboxylic acid in the 193-nm resist polymer. The continuing quest for higher resolution by using even shorter wavelengths has recently prompted a massive research effort in developing chemical amplification resists for use at 157 nm (F_2 excimer laser), which is essentially a search for a transparent and base-soluble functionality [6–8].

Each generation of new lithographic technologies has demanded new transparent polymer structures, while the use of a 0.26 N tetramethylammonium hydroxide (TMAH) developer originally optimized for the novolac/diazoquinone resist has always been imposed on new resist systems built on totally different polymer backbones and acidic groups with different pK_a . This paper describes the dissolution behavior of the polymers in chemical amplification resists designed for use in the three generations of the photolithographic technologies.

Polyhydroxystyrene derivatives in 248-nm resists

Poly(4-hydroxystyrene) (PHOST) is the resin on which 248-nm chemically amplified resists are based. It provides UV transparency (optical density = $\sim 0.2/\mu\text{m}$ at 248 nm), high dry-etch resistance, and aqueous base solubility. To render it insoluble in aqueous base and to achieve a chemically amplified polarity change, PHOST is partially protected with an acid-labile group such as *t*-butoxy-carbonyl (tBOC), as exemplified by APEX [9], or an acetal/ketal group, as found in KRS [10] or ARCH [11]. Another approach is copolymerization of 4-hydroxystyrene (HOST) with *t*-butyl acrylate (TBA), which is employed in preparation of the ESCAP resist resin [12]. Although PHOST is an isomer of the novolac resin, its dissolution rate in aqueous base is much faster. Therefore, the use of the industry-standard 0.26 N developer optimized for the novolac resist was initially thought to degrade the performance of PHOST-based 248-nm resists. However, the 248-nm resists currently on the market have been designed to be compatible with the strong developer [2(a)] and are capable of 125-nm line/space resolution.

Figure 1 presents the dissolution kinetics curves of PHOST with number-average molecular weight (M_n) ranging from 2300 to 26000 (as determined by gel permeation chromatography using polystyrene as a standard) and polydispersity (PD) of 1.2–5.5 in a 0.21 N TMAH developer. A quartz crystal microbalance (QCM) was employed in all dissolution measurements [13]. The narrow- PD polymers were prepared by living radical polymerization [14]. These narrow- PD polymers were blended to provide tandem molecular weight distributions ($PD = 5.5$) in some cases [14, 15]. One of the major findings of this work was that irrespective of M_n or PD ,

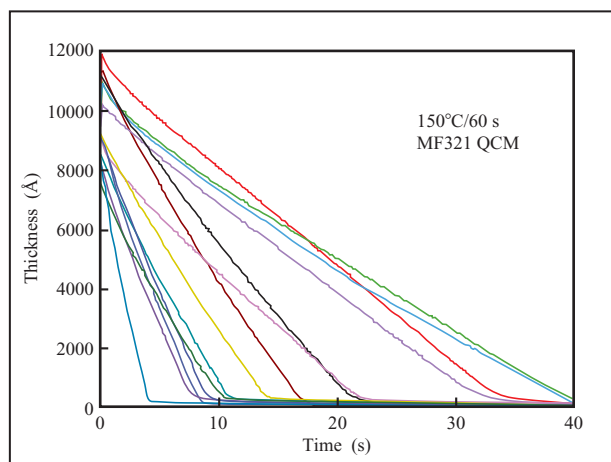


Figure 1

Dissolution kinetics of PHOST films ($M_n = 2300\text{--}26\,000$, $PD = 1.2\text{--}5.5$) in 0.21 N TMAH.

dissolution is highly linear with time [16, 17]. Even the blends with tandem molecular weight distributions dissolve at constant rates. **Figures 2 and 3** show the dissolution rates of the PHOST films as a function of M_n and weight-average molecular weight (M_w), respectively, for polymers with narrow and broad PD . The dissolution rate decreases exponentially and rapidly with increasing molecular weight when M_n is less than $\sim 10\,000$ ($M_w < \sim 15\,000$). Above these values the effect of molecular weight on the dissolution rate is negligible. The threshold-like molecular weight dependence of the dissolution rate is more pronounced in the case of narrow- PD polymers. The broad- PD polymers exhibit a more gradual change of the dissolution rate when the molecular weight is changed. Furthermore, the narrow- PD polymers tend to dissolve more slowly than the broad- PD polymers, especially in the molecular weight range of $M_n = 3000\text{--}15\,000$. Interestingly, the M_n of PHOST commonly employed in resist formulations falls in this range. A closer examination of Figures 2 and 3 reveals that the PD effect is much more significant in the M_w plot (Figure 3). In the M_n plot (Figure 2), the difference between the narrow- and broad- PD polymers is very small, which suggests that the dissolution rate of PHOST can be correlated with M_n in a more 1:1 fashion than with M_w . This observation in turn suggests that the dissolution of PHOST in aqueous base is controlled by lower-molecular-weight fractions, which represents a sharp contrast to the novolac systems [18]. We carried out a study of the dissolution rates of various blends made with narrow- PD PHOSTs which indicates that the dissolution rate of PHOST can be predicted from M_n irrespective of M_w or PD and suggests

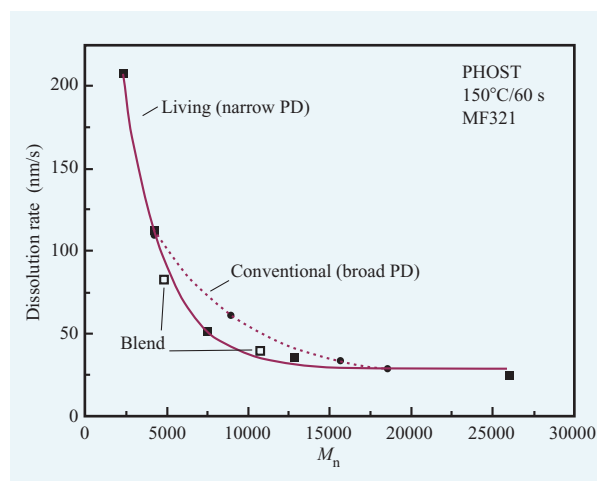


Figure 2

Effect of M_n on dissolution rate of PHOST in 0.21 N TMAH.

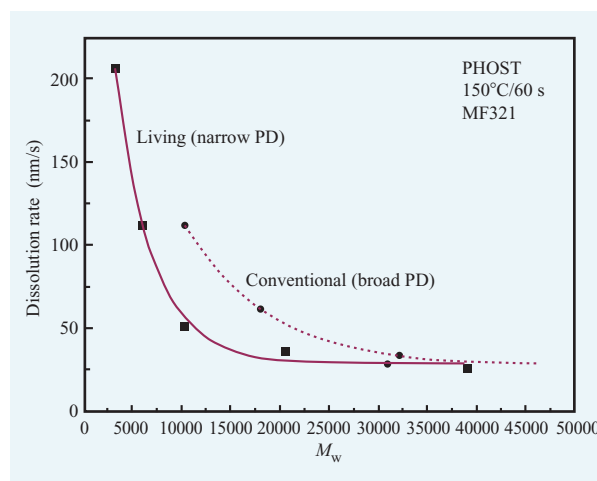


Figure 3

Effect of M_w on dissolution rate of PHOST in 0.21 N TMAH.

that the dissolution rate of PHOST in aqueous base is governed primarily by the lower-molecular-weight fractions.

The dissolution rates of all of the PHOST systems (narrow- and broad- PD polymers and blends) with PD ranging from 1.3 to 5.5 plotted against M_w in a log-log scale indicate that there is no straightforward relationship between the dissolution rate and M_w . In contrast, a similar plot of the dissolution rates of PHOST vs. M_n can be nicely expressed by an exponential decay (linear log-log

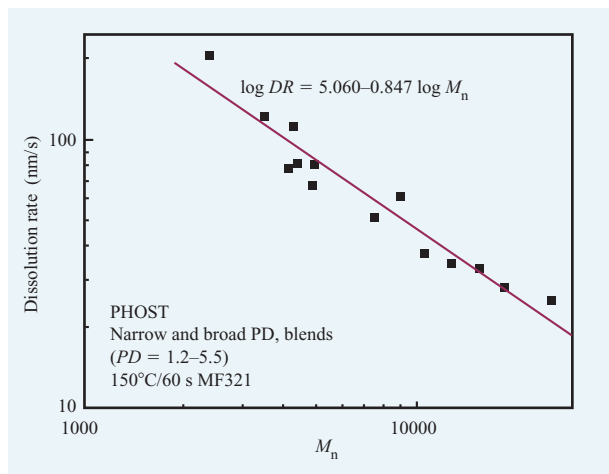


Figure 4

Dependence of dissolution rate on M_n of PHOST.

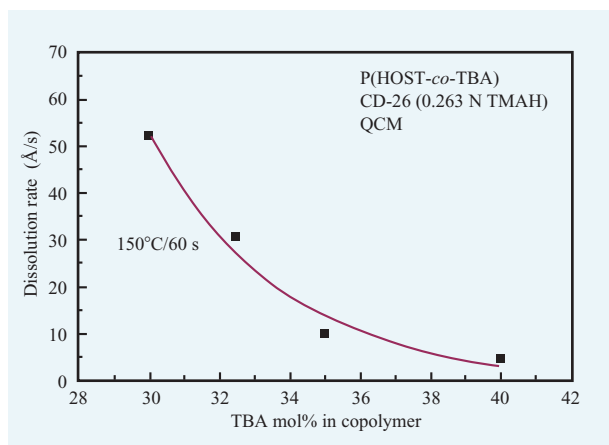


Figure 5

Dissolution rate of P(HOST-*co*-TBA) in CD-26 as a function of copolymer composition.

plot, as shown in **Figure 4**), even in a wide range of PD . Thus, M_n is a more meaningful parameter in characterizing the dissolution rate of PHOST. The dissolution rate of PHOST can be estimated if M_n is known. Although the molecular weights reported in this paper are relative to polystyrene, our discussion is valid because it deals only with mutual comparison of PHOST.

Since PHOST dissolves in aqueous base much more rapidly, it is more difficult to reduce its dissolution rate to a usable range by adding a lipophilic dissolution inhibitor than a novolac resin. Thus, the 248-nm resist polymers are prepared by partially protecting PHOST with a lipophilic

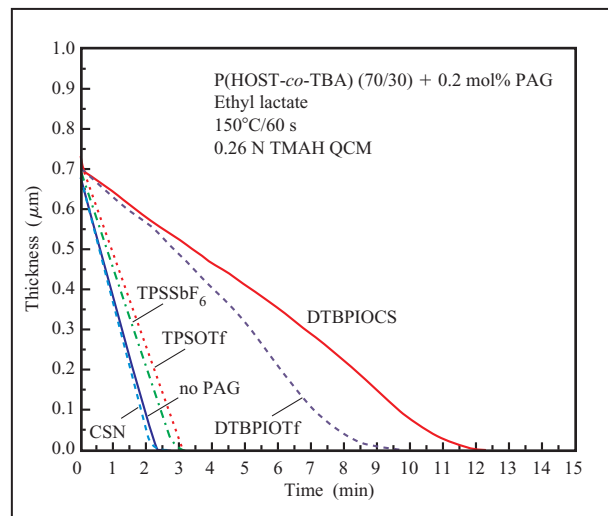


Figure 6

Dissolution kinetics of P(HOST-*co*-TBA) (70/30) containing 0.2 mol% PAG in 0.26 N TMAH.

acid-labile group or by copolymerizing HOST with TBA. P(HOST-*co*-TBA) is the resin used in the ESCAP resist and a foundation for many positive resists on the market [19]. The influence of the copolymer composition on its dissolution rate is shown in **Figure 5** [16, 17]. The dissolution rate becomes exponentially smaller as the TBA concentration in the copolymer increases. The dissolution rate change in CD-26 is insignificant above 35 mol% TBA. The small scatter in the plot may be due to the molecular weight variation ($M_n = 20200, 17600, 11200$, and 14400). Thus, for a minimal thinning in the unexposed area during development, the copolymer must contain less than 65 mol% HOST.

Certain photochemical acid generators (PAGs) are excellent dissolution inhibitors of phenolic resins [20]. **Figure 6** presents dissolution kinetics curves of P(HOST_{0.7}-*co*-TBA_{0.3}) containing 0.2 mol% PAG. The films were baked at 150°C for 60 s prior to dissolution measurements by QCM in CD-26. It is clear that onium salts such as di(4-*t*-butylphenyl)iodonium camphorsulfonate (DTBPIOCS) and triflate (DTBPIOTf) are strong dissolution inhibitors, whereas non-ionic *N*-camphorsulfonyloxynaphthalimide (CSN) is neutral, and that the inhibition effect depends on the onium salt structure [17]. **Figure 7** shows dissolution rates in CD-26 of the copolymers with varying composition as a function of the loading of triphenylsulfonium triflate (TPSOTf). The rate becomes exponentially smaller with an increasing TPSOTf concentration, especially when the rate is high. Figure 7 indicates that the addition of a small amount of TPSOTf gives a larger inhibition effect and that a loading above 5 wt% does not slow the dissolution rate further.

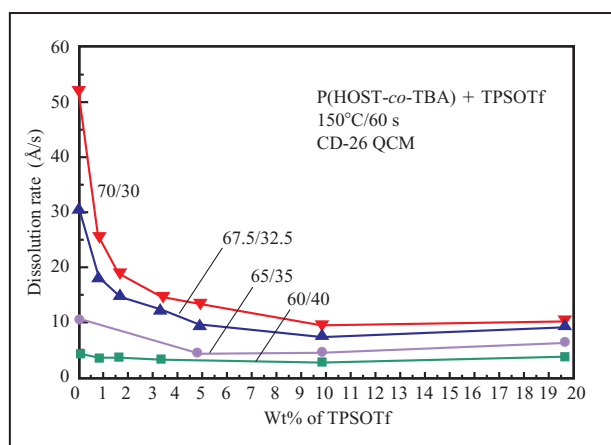


Figure 7

Dissolution rate in CD-26 of P(HOST-co-TBA) as a function of copolymer composition and TPSOTf loading.

The dissolution-inhibition effect of TPSOTf is larger when the dissolution rate is faster. Since the dissolution rate of the 60/40 copolymer is already quite slow because of the high concentration of the TBA unit, the addition of TPSOTf reduces its rate only slightly (by 30% at most) in CD-26. In the case of the rapidly dissolving 70/30 copolymer, the reduction of the dissolution rate by the addition of TPSOTf amounts to as much as 80%.

Certain onium salt PAGs function like diazonaphthoquinone; in addition to the dissolution-inhibition effect in the unexposed region, photolysis of certain PAGs results in an increase in the dissolution rate [20]. **Figure 8** depicts the effect of exposure on the dissolution rate of a PHOST ($M_n = 9100$ and $M_w = 18200$) film containing 5 wt% of di(4-*t*-butyl-phenyl)iodonium nonaflate (DTBPIONf) in CD-26. A film was prebaked at 150°C for 60 s and subjected to a QCM measurement. The second film, baked under the same conditions, was exposed to 48 mJ/cm² of 254-nm radiation and postexposure-baked at 135°C for 90 s. The faster dissolution rate of the exposed film is evident. When the exposed film was baked at a higher temperature (150°C in this case), however, significant swelling (followed by peeling) was observed, suggesting cross-linking. The positive-tone 248-nm resists ESCAP and APEX exhibit a negative (cross-linking component) at high exposure doses (high acid concentrations), especially when a strong acid such as nonaflc acid is generated and the PEB temperature is high [21]. Although the protecting group can play a role in the negative behavior [22], the PHOST-based resist systems can have an inherent negative component (cross-linking or molecular weight increase).

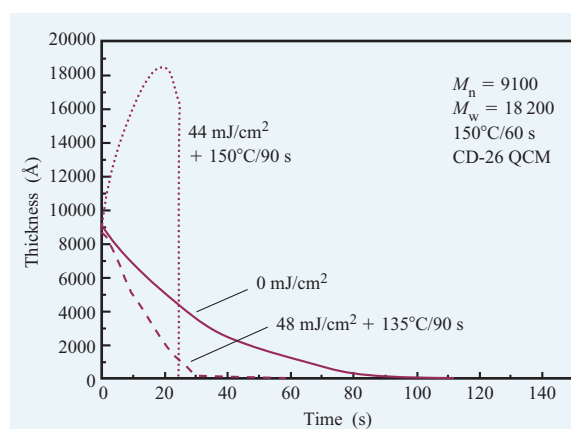
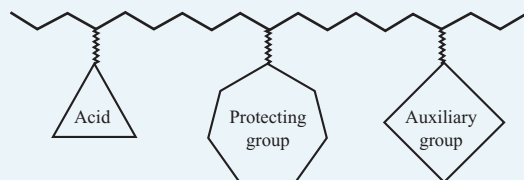


Figure 8

Dissolution kinetics in CD-26 of PHOST ($M_n = 9100$ and $M_w = 18200$) containing 5 wt% DTBPIONf prebaked at 150°C for 60 s, exposed to 48 mJ/cm² and postbaked at 135°C for 90 s, and exposed for 44 mJ/cm² and postbaked at 150°C for 90 s.

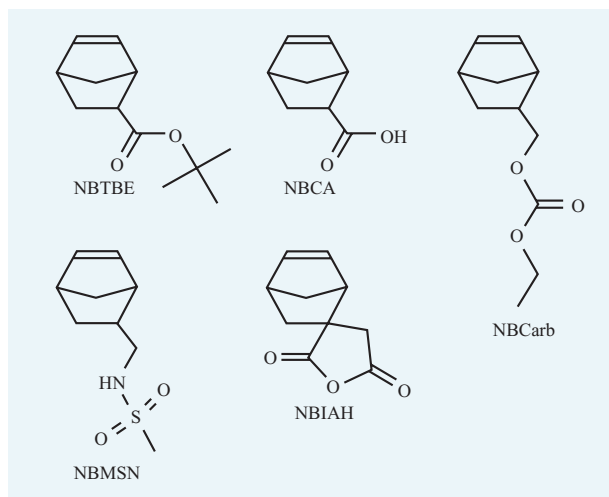


Scheme II

Positive resist design.

Polynorbornene derivatives in 193-nm resists

Polymers of functionalized norbornenes, prepared by transition-metal-initiated addition polymerization [23] or radical copolymerization with maleic anhydride (MA), are the major platforms on which 193-nm resist systems are built. The design strategy developed for the advanced 248-nm resists has been adopted; the resist polymer consists of a unit bearing a base-soluble acidic group and a unit containing an acid-labile protecting group (**Scheme II**). While the acid-labile group is in many cases a *tertiary* ester, the acidic functionality employed in the 193-nm system is carboxylic acid, which does not absorb at 193 nm in contrast to the phenol structure. Because the functionality of carboxylic acid is stronger than that of phenol in terms of acidity (pK_a 6 vs. 11), the aqueous development process had to be re-addressed. For example, the IBM Version 1 193-nm resist [24] based on a terpolymer of methacrylic acid, *t*-butyl methacrylate, and



Scheme III

Functionalized norbornene monomers used to prepare polycycloolefins for 193-nm resists.

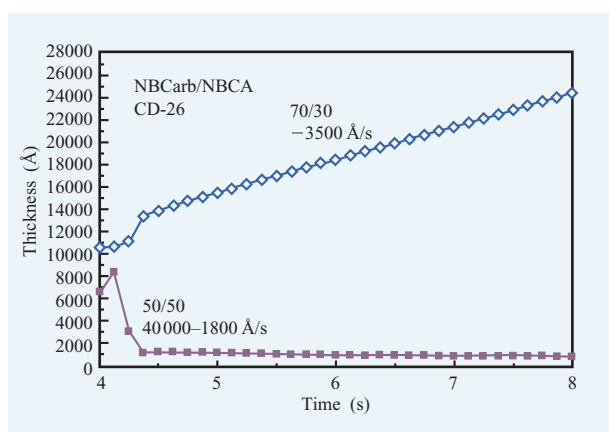


Figure 9

QCM kinetics curves of P(NBCarb-co-NBCA) in CD-26.

methyl methacrylate, which had been developed as a tool-testing resist, employed a very weak aqueous base (0.05 N) developer and was incompatible with the industry-standard 0.26 N developer. Incorporation of the carboxylic acid into polynorbornene has exhibited a profound effect on the dissolution behavior [25], which is described in this section.

Some norbornene (NB) monomers employed to prepare polycycloolefins are shown in **Scheme III** [25]. QCM kinetics curves of copolymers of 5-(ethoxycarbonyloxy)methyl-2-norbornene (NBCarb) and bicyclo[2.2.1]hept-2-ene-5-carboxylic acid (NBCA)

Table 1 Dissolution/swelling rate of cycloolefin polymers in CD-26.

Polymer composition	Rate* (Å/s)
NBCarb/NBTBE/NBCA = 20/60/20	-1.6
NBCarb/NBTBE/NBCA = 30/50/20	-5.4
NBCarb/NBCA = 70/30	-3500
NBCarb/NBCA = 60/40	-∞
NBCarb/NBCA = 50/50	42000-15700
NBCarb/NBCA = 40/60	16000-13700
NBCarb/NBCA = 30/70	17400-13000

*150°C/60-s bake; -: swelling, +: dissolution, -∞: massive swelling beyond QCM capability.

containing 30 and 50 mol% carboxylic acid in CD-26 are presented in **Figure 9**, illustrating the rather bizarre behavior of the cycloolefin polymer films in aqueous base. The ethyl carbonate pendant group was meant to be a polar modifier to tame the wild swelling behavior of the copolymer of NBTA with *t*-butyl bicyclo[2.2.1]hept-2-ene-5-carboxylate (NBTBE) and used as a comonomer with the ester and acid monomers (Scheme II). In order to better understand the influence of the third component on development, simple nonimageable copolymers such as the ones shown in Figure 9 were studied. The carbonate/acid copolymer containing 30 mol% acid swelled rapidly in CD-26 at a rate of 3500 Å/s. An increase in the carboxylic acid concentration from 30 to 50 mol% resulted in rapid dissolution at >18000 Å/s. The compositions between the two extreme cases shown in Figure 9 did not provide the intermediate dissolution behavior but induced massive swelling. The 60/40 copolymer film swelled beyond the capability of QCM. There is no smooth change of the dissolution rate as a function of composition; only insoluble, massively swelling, or extremely fast dissolution regimes exist. **Table 1** summarizes dissolution or swelling rates in CD-26 of cycloolefin copolymer and terpolymer films baked at 150°C for 60 s. Another example is presented in **Figure 10**. The copolymers of NBTBE with *N*-(5'-norbornene-2'-methyl)methanesulfonamide (NBMSN) did not dissolve or swell in CD-26 in a wide compositional range of 70/30 to 20/80, indicating that the acidic methanesulfonamide functionality does not provide a high enough affinity of the NBTBE polymer to an aqueous base developer in this case. Replacement of 10 mol% of NBTBE with NBTA resulted in significant swelling at a rate of 37 Å/s. Thus, the introduction of only 10 mol% of NBTA moved the polymer into a swelling regime in this case. The NBMSN-NBCA copolymers containing 30 or 40 mol% NBTA exhibited extreme swelling. The NBTA concentration in the addition polymers must typically be greater than 50 mol% to induce clean dissolution, although the threshold value

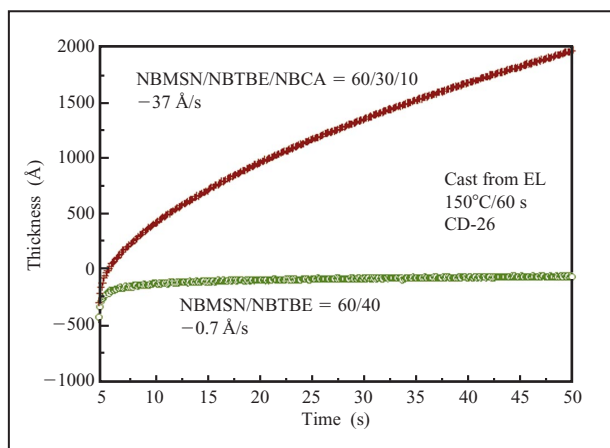


Figure 10

QCM kinetics curves of P(NBMSN-NBTBE-NBCA) in CD-26.

can vary depending on the polarity of the other monomer units. We have investigated other monomers in an attempt to control the dissolution rate or suppress the swelling, but an abrupt change from the insoluble state to extremely fast dissolution through a massive swelling regime was the common characteristic.

We extensively employed a polymer that swells massively at a *measurable* rate (such as the copolymer of NBCarb/NBCA = 70/30) in our studies on the additive effect, fundamental understanding of the swelling behavior, etc. **Figure 11** shows the effect of film thickness on the degree and rate of swelling, employing the carbonate/acid copolymer. Rapid swelling followed by abrupt cessation is a characteristic feature common to essentially all of the cycloolefin polymers we investigated. The maximum swelling is a function of film thickness; about 135% of thickness is added to the initial thickness due to swelling at the same rate of 3300–3400 Å/s in this case. The entire film thickness swells rapidly in a few seconds, and the swelling stops as soon as the aqueous base reaches the substrate interface.

As mentioned earlier, the swelling in the unexposed region can be eliminated and the dissolution in the fully exposed area can be maximized simply by adjusting the polymer composition. Unfortunately, however, a partial exposure occurs at the line edge in photolithography according to the modulation transfer function of the exposing light intensity. Thus, swelling of the partially exposed area remains a problem. The addition of so-called dissolution inhibitors dramatically reduces the undesired swelling and improves lithographic performance. In our case additional dissolution inhibition is not needed, and additives known as dissolution modifying agents (DMAs) are used. Such additives also function as plasticizers in

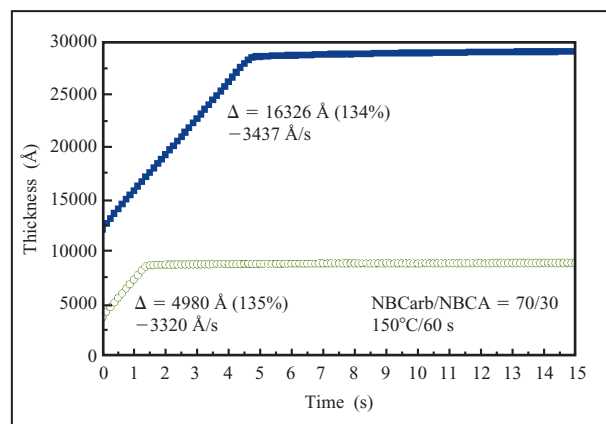


Figure 11

Effect of film thickness on swelling kinetics of P(NBCarb-co-NBCA) (70/30) in CD-26.

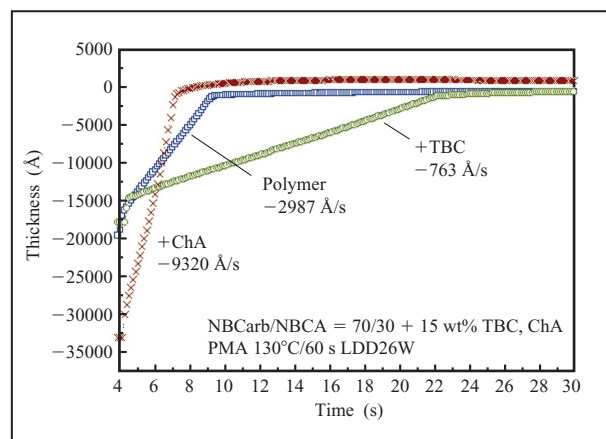


Figure 12

Effects of TBC and ChA addition on swelling kinetics of P(NBCarb-co-NBCA) (70/30) in LDD26W.

some cases. A classical example is *t*-butyl cholate (TBC) [26], which is converted to cholic acid (ChA) upon reaction with a photochemically generated acid. We have investigated a number of active and passive DMAs [27] and present TBC as an example in this paper. Since an active DMA such as TBC is converted to carboxylic acid (ChA) in the polymer film, we also investigated the influence of the acid form of DMAs on the dissolution/swelling behavior.

The effect of a DMA can be most dramatically and clearly observed by employing a cycloolefin polymer that swells at a significant but measurable rate. **Figure 12** shows QCM curves generated in LDD26W (0.26 N

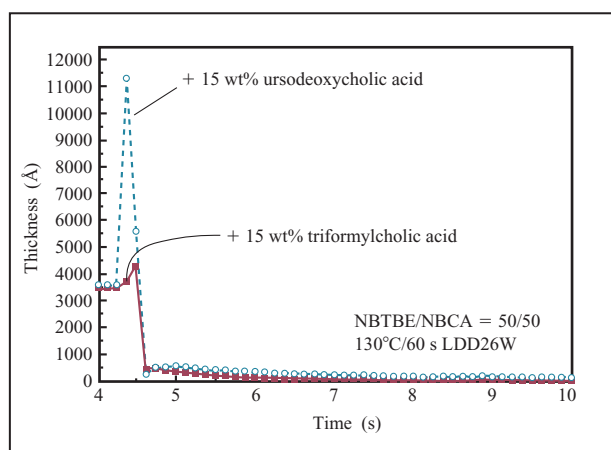


Figure 13

Dissolution promotion of massively swelling P(NBTBE-*co*-NBCA) (50/50) by addition of cholic acid derivatives.

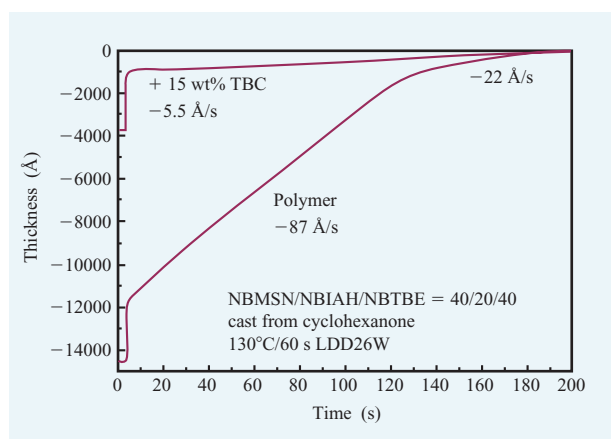


Figure 14

Effect of addition of TBC on swelling of P(NBMSN-NBIAH-NBTBE) (40/20/40) in LDD26W.

TMAH) for the NBCarb/NBCA = 70/30 copolymer and the same film containing 15 wt% TBC. In this case the films were baked at 130°C for 60 s. While the polymer film swelled at ~ 3000 Å/s, the addition of TBC suppressed the swelling rate to 760 Å/s. However, the maximum swelling, which is a function of thickness, was unaffected. In contrast, the addition of 15 wt% ChA significantly increased the swelling rate from 3000 to 9300 Å/s, as Figure 12 demonstrates. Thus, the function of active DMA is dynamic and complex; the extent of acidolysis matters for both the polymer and the DMA. Another swelling

polymer employed in our study was a terpolymer of NBMSN/NBTBE/NBCA = 40/40/20, which swelled at 1300 Å/s in LDD26W when baked at 130°C for 60 s, at 76 Å/s in the presence of 15 wt% TBC, and at 2750 Å/s when doped with 15 wt% ChA. Different DMAs and different carboxylic acids exhibit different effects on the dissolution/swelling behavior of cycloolefin polymers.

Figure 13 presents a dissolution-promotion effect of some cholic acid derivatives. The 50/50 copolymer of NBTBE and NBCA exhibits extreme swelling beyond the capability of our QCM. However, the addition of 15 wt% of ursodeoxycholic acid or triformylcholic acid to this polymer resulted in fast dissolution in LDD26W, although initial swelling was evident, especially with the latter acid. Such dissolution promotion is required to make DMA work lithographically. Furthermore, photochemically generated sulfonic acids could also affect the dissolution/swelling behavior of the cycloolefin polymers.

We have not fully understood the constructive interaction of DMA with the matrix polymer during the development step. However, the cycloolefin resist can demonstrate excellent lithographic performance when the formulation (polymer structure, polymer composition, DMA selection, DMA loading, PAG, etc.) and process conditions are optimized [28].

The NB-MA copolymers have provided a quick entry to high-resolution imaging, suggesting an attractive feature associated with the anhydride structure. The anhydride structure was incorporated into addition polymers in several ways [25]. One approach was to utilize an NB monomer bearing a spiroanhydride structure prepared by the Diels-Alder reaction involving itaconic anhydride (NBIAH, Scheme III). A variety of copolymers and terpolymers containing NBIAH have been synthesized. One example was a terpolymer of NBIAH, NBTBE, and NB with pendant methanesulfonamide (NBMSN, Scheme III). Although the sulfonamide structure was expected to provide base solubility [29], NBTBE copolymers containing up to 80 mol% NBMSN did not dissolve (or swell) at all in CD-26. In the presence of NBCA, this sulfonamide functionality was a promoter of swelling. The NBMSN/NBIAH/NBTBE terpolymer (40/20/40) swelled at 87 Å/s in LDD26W after baking at 130°C for 60 s (**Figure 14**). The faster swelling of the terpolymer than the NBMSN/NBTBE copolymers was suspected to be due to hydrolysis of the anhydride ring during base development. Certain protecting groups have been assumed to be converted to carboxylic acid during base development [30]. Anhydrides are known to undergo base hydrolysis rapidly in solution. Investigation of base hydrolysis under the condition mimicking the development process as closely as possible was critically important. A 1-in. undoped Si wafer was coated with a polymer film, baked at 130°C for 60 s,

and covered with a meniscus of water on which another undoped Si wafer was placed. The excess water was squeezed out, and the sandwich sample was subjected to transmission FT-IR analysis using an undoped Si wafer as a blank. It is generally difficult to measure an infrared (IR) spectrum in water because of the large absorption obscuring the carbonyl region (**Figure 15**). Fortunately, however, the anhydride IR absorptions appear outside the water envelope, allowing us to monitor the hydrolysis. In a similar fashion, a sample was prepared, replacing water with an aqueous base developer such as CD-26. Typically about two minutes elapsed between application of the developer (or pure water) and recording an IR spectrum. Figure 15 clearly indicates that the anhydride absorptions have completely disappeared after the base treatment. This study has for the first time demonstrated that the anhydride hydrolysis can take place in the solid film upon contact with aqueous developer within the time scale of development. The sulfonamide functionality is not acidic enough in the polycycloolefin to induce dissolution, but it is polar enough to allow penetration of the aqueous developer, which induces hydrolysis of anhydride, promoting swelling. Aqueous base penetration is believed to be the most important step in base hydrolysis of anhydride during development, which is essentially controlled by the polarity of the matrix. A number of experiments were carried out to prove the polarity effect on hydrolysis. One example is shown in **Figure 16**. The same NBMSN/NBIAH/NBTBE film was doped with 15 wt% of TBC DMA, and similar IR measurements were performed. The terpolymer film containing lipophilic TBC did not allow hydrolysis of the anhydride upon base treatment, presumably because of limited aqueous base penetration into the film. Thus, swelling was suppressed from 87 to 5.5 Å/s by adding TBC (Figure 16). In this case the DMA additive functions as a barrier to base penetration and as a protector of anhydride from hydrolysis.

Thus, the hydrolysis of anhydride during development can increase the development contrast if it is induced selectively only in the exposed regions, which is typically the case because more carboxylic acid is generated through deprotection and more interaction with the developer takes place in the exposed areas. The alternating NB-MA copolymers tend to provide good lithographic performance for this reason. However, the anhydride hydrolysis could cause some problems as well. Without intentional incorporation of carboxylic acid, the NB-MA copolymers tend to contain a small concentration of carboxylic acid due to anhydride hydrolysis during workup. Upon standing at room temperature, the hydrolysis proceeds and the solution ages, resulting in much faster dissolution in aqueous base (for example, from 7.9 to 524 Å/s in one year). Because of the

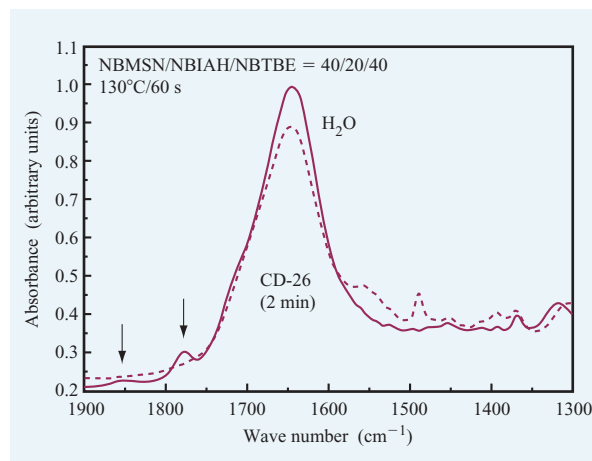


Figure 15

Base hydrolysis of anhydride in P(NBMSN-NBIAH-NBTBE) (40/20/40) in CD-26 as studied by Fourier transform infrared spectroscopy.

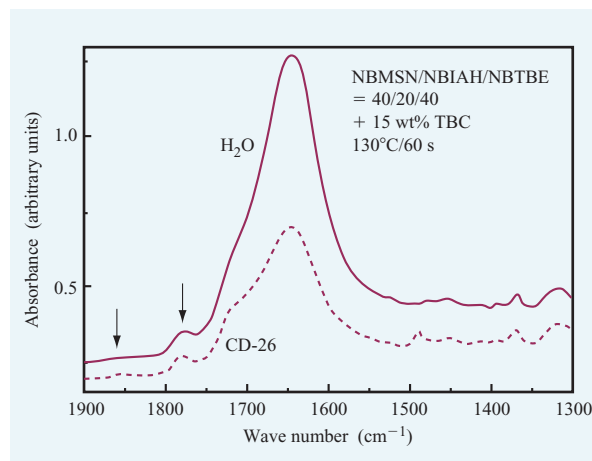
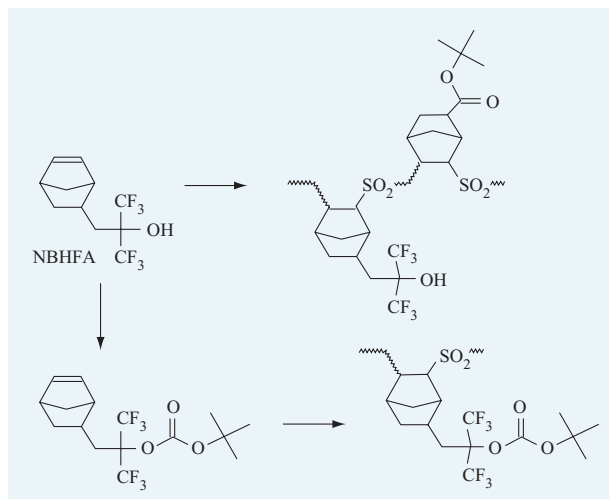


Figure 16

Suppression of base hydrolysis of anhydride in P(NBMSN/NBIAH/NBTBE) (40/20/40) by addition of TBC as studied by *in situ* IR analysis.

unintended presence of carboxylic acid, base hydrolysis with TMAH can take place in the NBTBE-MA polymer film during development. The hydrolysis can be completed within a couple of minutes in CD-26. Thus, the NB-MA resist could exhibit undesirable thinning in the unexposed region, which could be accelerated as the resist solution ages. For this reason, intentional incorporation of carboxylic acid in the NB-MA polymer must be dealt with cautiously. This approach would definitely require incorporation of a hydrophobic additive as an anhydride



Scheme IV

Acidic hexafluoroisopropanol pendant from norbornene.

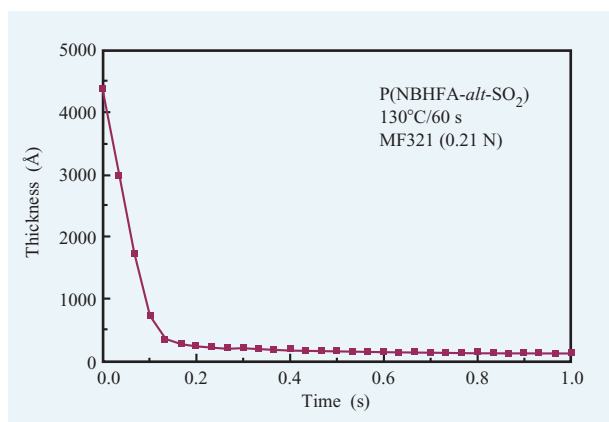


Figure 17

Dissolution kinetics of P(NBHFA-*alt*-SO₂) in 0.21 N TMAH.

protector rather than as a dissolution inhibitor. One of the 193-nm resist systems is based on the NB-MA terpolymer involving acrylic acid as a third monomer in conjunction with the use of cholate derivatives [31]. The lipophilic cholates could suppress base penetration, protect anhydride, and reduce undesirable thinning in the unexposed area.

Hexafluoroalcohol functionality for 193- and 157-nm resists

Considering the high performance of resist systems built on the phenolic functionality and the strong swelling tendency associated with the carboxylic acid polymers,

we were interested in another acidic group which has a pK_a similar to that of phenol but is transparent below 200 nm. According to the literature [32], the pK_a of trifluoromethylcarbinol derivatives varies from 6.7 [(CF₃)₃COH] (similar to 6.3 of acetic acid) to ~11 [11.2 for (CF₃)₂CHOH and 11.5 for (CF₃)₂CH₂COH] (similar to 11.8 of phenol). Thus, we became interested in utilizing the (CF₃)₂COH moiety as a base-soluble functionality. We incorporated the fluoroalcohol structure into norbornene and copolymerized the norbornene monomer, bicyclo[2.2.1]hept-5-ene-2-(1,1,1-trifluoro-2-trifluoromethylpropano-2-ol) (NBHFA), with sulfur dioxide by radical initiation to form an alternating copolymer (**Scheme IV**) [29]. We also carried out radical terpolymerization of NBHFA, NBTBE, and SO₂, varying the ratio of NBTBE to NBHFA (**Scheme IV**), and analyzed the terpolymer composition by inverse-gated ¹³C NMR [29].

The dissolution behavior of P(NBHFA-*alt*-SO₂) (M_n = 3800 and M_w = 6500) was studied on QCM in a 0.21 N TMAH solution using thin films cast from ethyl lactate and baked at 130°C for 60 s. **Figure 17** presents the dissolution kinetics curve of the polysulfone film. The 450-nm-thick film dissolved away in 0.15 s, with an extremely fast dissolution rate of 30000 Å/s. The dissolution rate of PHOST in the same 0.21 N developer is in the range of 3000–200 Å/s depending on its molecular weight, as discussed earlier [15]. Thus, the fluoroalcohol polymer dissolves at least one order of magnitude faster than PHOST, which was unexpected considering the similar pK_a values of the fluoroalcohol and phenol. In addition to pK_a , the dissolution rate in aqueous base is very much affected by the degree of hydrogen bonding, polymer backbone structure, free volume in the film, etc. The rigid backbone structure of the poly(norbornene sulfone) may be responsible, at least in part, for the fast dissolution rate.

The dissolution rates of the NBHFA-NBTBE-SO₂ terpolymer films were measured under the same conditions (bake: 130°C for 60 s; developer: 0.21 N TMAH) and plotted in **Figure 18** as a function of the terpolymer composition. As NBTBE is introduced into the polymer, the molecular weight becomes larger and the dissolution rate exponentially smaller. The dissolution rate for NBHFA/NBTBE = 1/1 is ~170 Å/s, and the terpolymers with more than 55 mol% *t*-butyl ester do not dissolve at all in this developer. It thus appears that the concentration of the fluoroalcohol unit in the terpolymer must be less than 45% for an unexposed resist film in order to provide minimum thinning in the industry-standard 0.26 N TMAH solution. What is noteworthy is that the fluoroalcohol group does not seem to induce swelling in the poly(norbornene sulfone). This fluoroalcohol functionality has become the acid group of choice for the design of 157-nm resist systems [6, 8].

Experimental section

Materials

The preparation procedures for PHOST [14, 15] and P(HOST-*co*-TBA) [12] are found elsewhere. The functionalized polynorbornenes were prepared and purified at the BFGoodrich Company [23]. Poly(norbornene-*co*-maleic anhydride) was prepared by radical copolymerization using 2,2'-azobis(isobutyronitrile) in tetrahydrofuran at 60°C [29]. The synthesis and polymerization of NBHFA have been reported in the literature [29]. The casting solvents employed in this study were propylene glycol methyl ether acetate, ethyl lactate, or cyclohexanone.

Measurements

Quantitative ^{13}C NMR spectra were obtained for some of the polymers in acetone- d_6 to determine their compositions in an inverse-gated ^1H -decoupled mode using chromium (III) acetylacetonate [$\text{Cr}(\text{acac})_3$] as a relaxation agent on a Bruker AF250 at room temperature, AC300 at 61°C, and AM500 at room temperature. IR spectra were recorded on a Nicolet Magna-IR 550 spectrometer on a film cast on a KBr or NaCl plate or undoped Si wafer. Molecular weight determination was made by gel permeation chromatography (GPC) using a Waters Model 150 chromatograph equipped with four ultrastaygel columns at 40°C in THF, using polystyrene as a standard. A quartz crystal microbalance (QCM) was used to study the kinetics of dissolution or swelling of the polymer films in an aqueous developer [14–17, 25]. The crystals employed in this study had an inherent frequency of about 5 MHz. Quartz crystal discs with gold contacts were coated with polymer films, baked at 130–150°C for 60 s, and mounted on a sensor probe. A Maxtek TPS-550 sensor probe and PI-70 driver were used in conjunction with a Phillips PM6654 programmable high-resolution frequency counter and an IBM PC. The instrumentation was controlled and data collected by a custom-made LabView software program.

Conclusions

The dissolution behavior of chemically amplified resist polymers in aqueous base developer was investigated using a quartz crystal microbalance. PHOST employed in 248-nm resist formulations dissolves in a more or less linear fashion. Its logarithmic dissolution rate decreases linearly with increasing logarithmic M_n . The dissolution rate of HOST-TBA copolymers is a monotonous function of the copolymer composition, which is significantly lowered by the addition of ionic acid generators. The strong dissolution-inhibition effect of certain onium salt acid generators must be taken into consideration in resist

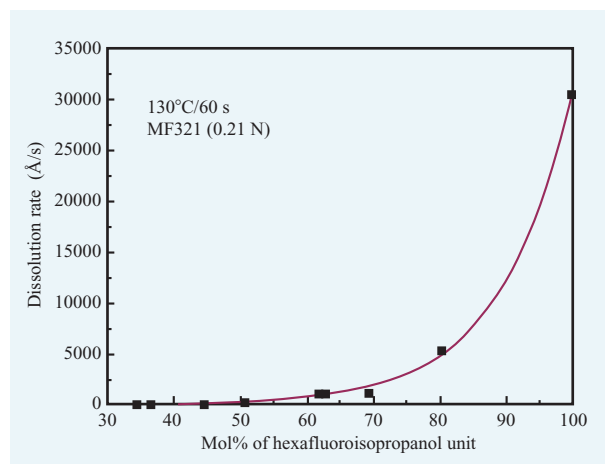


Figure 18

Dissolution rate of terpolymer of NBHFA, NBTBE, and SO_2 in 0.21 N TMAH as a function of polymer composition.

formulation. PHOST can undergo cross-linking when postexposure baked at high temperatures in the presence of a large amount of a strong perfluoroalkanesulfonic acid.

Polynorbornenes bearing pendant carboxylic acid for use in 193-nm resist formulation exhibit a dissolution behavior that is not a monotonous function of the copolymer composition. The copolymer film is insoluble in 0.26 N TMAH when the carboxylic acid concentration in copolymer is less than 20 mol% and dissolves very rapidly when the acid content is above 50 mol%. There is a massive swelling zone in a wide range of composition (typically $20 \text{ mol}\% < \text{acid} < 50 \text{ mol}\%$). The swelling rate can be reduced by addition of a dissolution-modifying agent such as *t*-butyl cholate. Anhydride structures incorporated in 193-nm resist polymers can undergo hydrolysis during aqueous base development when the matrix is polar enough to allow penetration of aqueous base into the film. Selective hydrolysis of anhydride in the exposed area during aqueous base development can increase contrast, but unwanted hydrolysis during storage of anhydride-containing polymers can shorten shelf life. The addition of a lipophilic dissolution inhibitor or dissolution-modifying agent can reduce aqueous base penetration and thus protect the anhydride ring from hydrolysis.

Hexafluoroisopropanol has a pK_a similar to that of phenol, and the dissolution rate of terpolymers of NBHFA, NBTBE, and SO_2 can be controlled by changing the composition. Because of its desirable dissolution behavior and high UV transparency, the hexafluoroisopropanol functionality has become the acid group of choice for the design of 157-nm chemically amplified resists.

References

1. R. R. Dammel, "New Developments in High-Performance Resist Materials," *J. Photopolym. Sci. Technol.* **11**, 687-704 (1998).
2. (a) H. Ito, "Deep UV Resists: Evolution and Status," *Solid State Technol.* **36**, 164-173 (1996); (b) H. Ito, "Chemical Amplification Resists: History and Development Within IBM," *IBM J. Res. & Dev.* **41**, 69-80 (1997).
3. (a) H. Ito, C. G. Willson, and J. M. J. Fréchet, "New UV Resists with Negative or Positive Tone," *Digest of Technical Papers of 1982 Symposium on VLSI Technology*, 1982, pp. 86-87; (b) H. Ito and C. G. Willson, "Chemical Amplification in the Design of Dry Developing Resist Materials," *Technical Papers of SPE Regional Technical Conference on Photopolymers*, 1982, pp. 331-353; (c) H. Ito and C. G. Willson, "Applications of Photoinitiators to the Design of Resists for Semiconductor Manufacturing," *ACS Symposium Series 242, "Polymers in Electronics,"* T. Davidson, Ed., American Chemical Society, Washington, D.C., 1984, pp. 11-23.
4. H. Ito, C. G. Willson, and J. M. J. Fréchet, "Positive- and Negative-Working Resist Compositions with Acid Generating Photoinitiator and Polymer with Acid Labile Groups Pendant from Polymer Backbone," U.S. Patent 4,491,628, 1985.
5. R. D. Allen, "Progress in 193 nm Photoresists," *Semicond. Int.* **20**, 73-80 (1997).
6. (a) K. Paterson, M. Yamachika, R. Hung, C. Brodsky, S. Yamada, M. Somerville, B. Osborn, D. Hall, G. Dukovic, J. Byers, W. Conley, and C. G. Willson, "Polymers for 157 nm Photoresist Applications: A Progress Report," *Proc. SPIE* **3999**, 365-374 (2000); (b) T. Chiba, R. J. Hung, S. Yamada, B. Trinque, M. Yamachika, C. Brodsky, K. Paterson, A. V. Heyden, A. Jamison, S.-H. Lin, M. Somerville, J. Byers, W. Conley, and C. G. Willson, "157 nm Resist Materials: A Progress Report," *J. Photopolym. Sci. Technol.* **13**, 657-664 (2000).
7. M. K. Crawford, A. E. Feiring, J. Feldman, R. H. French, M. Periyasamy, F. L. Schadt III, R. J. Smalley, F. C. Zumsteg, R. R. Kunz, V. Rao, L. Liao, and S. M. Holl, "New Materials for 157 nm Photoresists: Characterization and Properties," *Proc. SPIE* **3999**, 357-364 (2000).
8. (a) D. Schmaljohann, Y. C. Bae, G. L. Weibel, A. H. Hamad, and C. K. Ober, "Design Strategies for 157 nm Single-Layer Photoresists: Lithographic Evaluation of a Poly(α -trifluoromethyl Vinyl Alcohol) Copolymer," *Proc. SPIE* **3999**, 330-334 (2000); (b) D. Schmaljohann, Y. C. Bae, J. Dai, G. L. Weibel, A. H. Hamad, and C. K. Ober, "Fundamental Studies of Fluoropolymer Photoresists for 157-nm Lithography," *J. Photopolym. Sci. Technol.* **13**, 451-458 (2000).
9. R. L. Woods, C. F. Lyons, R. Mueller, and J. Conway, "Practical Half-Micron Lithography with a 10X KrF Excimer Laser Stepper," *Proceedings of the KTI Microelectronics Seminar*, 1988, pp. 341-359.
10. W.-S. Huang, R. Kwong, A. Katnani, and M. Khojasteh, "Evaluation of a New Environmentally Stable Positive Tone Chemically Amplified Deep-UV Resist," *Proc. SPIE* **2195**, 37-46 (1994).
11. C. Mertesdorf, N. Münzel, H. Holzwarth, P. Falcigno, H.-T. Schacht, O. Rohdem, R. Schulz, S. G. Slater, D. Frey, O. Nalamasu, A. G. Timko, and T. X. Neenan, "Structural Design of Ketal and Acetal Blocking Groups in 2-Component Chemically Amplified Positive DUV-Resists," *Proc. SPIE* **2438**, 84-98 (1995).
12. H. Ito, G. Breyta, D. Hofer, R. Sooriyakumaran, K. Petrillo, and D. Seeger, "Environmentally Stable Chemical Amplification Positive Resist: Principle, Chemistry, Contamination Resistance, and Lithographic Feasibility," *J. Photopolym. Sci. Technol.* **7**, 433-448 (1994).
13. W. D. Hinsberg, C. G. Willson, and K. K. Kanazawa, "Measurement of Thin-Film Dissolution Kinetics Using a Quartz Crystal Microbalance," *J. Electrochem. Soc.* **133**, 1448-1451 (1986).
14. G. G. Barclay, C. J. Hawker, H. Ito, A. Orellana, P. R. L. Malenfant, and R. F. Sinta, "The Living Free Radical Synthesis of Poly(4-hydroxystyrene): Physical Properties and Dissolution Behavior," *Macromolecules* **31**, 1024-1031 (1998).
15. G. G. Barclay, C. J. Hawker, H. Ito, A. Orellana, P. R. L. Malenfant, and R. F. Sinta, "Narrow Polydispersity Polymers for Microlithography: Synthesis and Properties," *Proc. SPIE* **2724**, 249-260 (1996).
16. H. Ito, D. Fenzel-Alexander, and G. Breyta, "Dissolution Behavior of Phenolic Resins and Resists as Studied by Quartz Crystal Microbalance," *Proc. SPIE* **3049**, 575-584 (1997).
17. H. Ito, D. Fenzel-Alexander, and G. Breyta, "Dissolution Kinetics and PAG Interaction of Phenolic Resins in Chemically Amplified Resists," *J. Photopolym. Sci. Technol.* **10**, 397-408 (1997).
18. P. C. Tsiartas, L. L. Simpson, A. Qin, C. G. Willson, and R. D. Allen, "Effect of Molecular Weight Distribution on the Dissolution Properties of Novolac Blends," *Proc. SPIE* **2438**, 261-271 (1995).
19. W. Conley, B. Brunsvold, F. Buehrer, R. Dellaguardia, D. Dobuzinsky, T. Farrell, H. Ho, A. Katnani, R. Keller, J. Marsh, P. Muller, R. Nunes, H. Ng, J. Oberschmidt, M. Pike, D. Ryan, T. Cotler-Wagner, R. Schulz, H. Ito, D. Hofer, G. Breyta, D. Fenzel-Alexander, G. Wallraff, J. Opitz, J. Thackeray, G. Barclay, J. Cameron, T. Lindsay, M. Cronin, M. Moynihan, S. Nour, J. Georger, M. Mori, P. Hagerty, R. Sinta, and T. Zydowsky, "New ESCAP-Type Resist with Enhanced Etch Resistance and Its Application to Future DRAM and Logic Devices," *Proc. SPIE* **3049**, 282-299 (1997).
20. H. Ito and E. Flores, "Evaluation of Onium Salt Cationic Photoinitiators as Novel Dissolution Inhibitor for Novolac Resin," *J. Electrochem. Soc.* **135**, 2322-2327 (1988).
21. (a) H. Ito and M. Sherwood, "NMR Analysis of Chemically Amplified Resist Films," *Proc. SPIE* **3678**, 104-115 (1999); (b) H. Ito and M. Sherwood, "Investigation of Deep UV Resists by NMR: Residual Casting Solvents, Chemistries, and PAG Decomposition in Film," *J. Photopolym. Sci. Technol.* **12**, 625-636 (1999).
22. T. Sakamizu, H. Shiraishi, H. Yamaguchi, T. Ueno, and N. Hayashi, "Acid-Catalyzed Reactions of Tetrahydropyranyl-Protected Polyvinylphenol in a Novolac-Resin-Based Positive Resist," *Jpn. J. Appl. Phys.* **31**, 4288-4293 (1992).
23. L. F. Rhodes, A. Bell, S. Jayaraman, J.-H. Lipian, B. L. Goodall, and R. A. Shick, "Photoresist Compositions Comprising Polycyclic Polymers with Acid Labile Pendant Groups," International Patent WO9914256, 1999.
24. R. R. Kunz, R. D. Allen, W. D. Hinsberg, and G. M. Wallraff, "Acid-Catalyzed Single-Layer Resists for ArF Lithography," *Proc. SPIE* **1925**, 167-175 (1993).
25. H. Ito, R. D. Allen, J. Opitz, T. I. Wallow, H. D. Truong, D. C. Hofer, P. R. Varanasi, G. M. Jordhamo, S. Jayaraman, and R. Vicari, "Dissolution/Swelling Behavior of Cycloolefin Polymers in Aqueous Base," *Proc. SPIE* **3999**, 2-12 (2000).
26. M. J. O'Brien, "Novolac-Based Photoresists Combining Chemical Amplification and Dissolution Inhibition," *Polym. Eng. Sci.* **29**, 846-849 (1989).
27. R. D. Allen, G. M. Wallraff, R. A. DiPietro, D. Hofer, and R. R. Kunz, "193 nm Single Layer Positive Resists: Building Etch Resistance into a High Resolution Imaging System," *Proc. SPIE* **2438**, 474-485 (1995).

28. P. R. Varanasi, J. Maniscalco, A. M. Mewherter, M. C. Lawson, G. Jordhamo, R. Allen, J. Opitz, H. Ito, T. Wallow, D. Hofer, L. Langsdorf, S. Jayaraman, and R. Vicari, "Design and Development of High Performance 193 nm Positive Resist Based on Functionalized Poly(cycloolefins)," *Proc. SPIE* **3678**, 51–63 (1999).
29. H. Ito, N. Seehof, R. Sato, T. Nakayama, and M. Ueda, "Synthesis and Evaluation of Alicyclic Backbone Polymers for 193 nm Lithography," *ACS Symposium Series* **706**, "Micro- and Nanopatterning Polymers," H. Ito, E. Reichmanis, O. Nalamasu, and T. Ueno, Eds., American Chemical Society, Washington, D.C., 1998, pp. 208–223.
30. I. L. Rushkin, F. M. Houlihan, J. M. Kometani, R. S. Hutton, A. G. Timko, E. Reichmanis, O. Nalamasu, A. H. Gabor, A. N. Medina, S. G. Slater, and M. Neisser, "New Polymers for 193 nm Single Layer Resists Based on Substituted Cycloolefins/Maleic Anhydride Resins," *Proc. SPIE* **3678**, 44–50 (1999).
31. F. M. Houlihan, T. Wallow, A. Timko, E. Neria, R. Hutton, R. Cirelli, J. M. Kometani, O. Nalamasu, and E. Reichmanis, "A Commercially Viable 193 nm Single Layer Resist Platform," *J. Photopolym. Sci. Technol.* **10**, 511–520 (1997).
32. J. R. Gandler and W. P. Jencks, "General Base Catalysis, Structure–Reactivity Interactions, and Merging of Mechanisms for Elimination Reactions of (2-Arylethyl)quinuclidinium Ions," *J. Amer. Chem. Soc.* **104**, 1937–1951 (1982).

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