Deep-UV Chemically Amplified Dissolution-Inhibited Photoresists

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A novel deep-UV photoresist has been developed with good sensitivity, resolution, and contrast. These characteristics were obtained using poly(4-hydroxystyrene-*co*-styrene) copolymers as the base resin together with *tert*-butyl cholate as a deblockable dissolution inhibitor. A triarylsulfonium salt photoacid generator was used in the photoresist to supply the strong acid required to deblock the dissolution inhibitor. The photoresist was imaged at 248 nm using an excimer laser stepper.

Introduction

Continued advances in microelectronics and photolithography have accelerated the demand for photoresists with ever higher photosensitivity and resolution capabilities. The current goal of the microelectronic industry is to develop integrated circuits with minimum features of less than 0.5 μm. It is well recognized that to accomplish this goal, exposure tools which operate in the deep UV region (190–365 nm) of the spectrum will have to be used. Today, the best irradiation source which has been developed for use in this region is the KrF excimer laser emitting at 248 nm.[1–3] Accordingly, most recent developmental photoresist efforts are being directed specifically to respond to this exposure tool. However, one problem with KrF excimer laser photolithography is the current lack of photoresist with high sensitivity and resolution.

To develop photoresists responsive to the 248 nm region, several major problems must be overcome. The first of these is the problem of achieving adequate sensitivity in this region of the electromagnetic spectrum. In recent years, a number of new materials have been developed which provide very high sensitivities as compared to conventional photoresists based on diazonaphthoquinone dissolution inhibited novolacs.[4,5] In general, these systems owe their high sensitivites to the achievement of chemical amplification, a process which ensures that each photoevent is used in a multiplicative fashion to generate a cascade of successive reactions. Although a number of different methods have been employed by a number of investigators,[6–10] this is most commonly accomplished through the use of photosensitive compounds which upon irradiation generate catalytic agents. In subsequent dark reactions, the catalysts induce many reaction events which ultimately result in a marked alteration of the solubility characteristics of the exposed photoresist. The overall effect is that the absorption of a single photon of light results in the chemical modification of a large number of molecules. Thus, the effect of the light can be said to have been "amplified" by the dark or nonphotochemical catalytic process. To achieve its inherent high sensitivity, only the photosensitive catalyst precursor of a chemically amplified photoresist must absorb in the region of interest. All the other components of the photoresist must be as transparent as possible in the same wavelength region.

In addition to a high sensitivity and resolution, a prospective deep UV photoresist must also possess a good transmittance at the desired exposure wavelength, have a positive tone, be developable in aqueous base, and have a good resistance toward reactive ion etching. Most current positive photoresist formulations are based on diazonaphthoquinone dissolution inhibitred novolac resins which have excellent reactive ion etch resistance, are positive tone resists, and allow development in aqueous base. However, because of their poor transmittance in the 248 nm region and their low photosensitivity at that wavelength, they cannot be used for deep UV photolithography.

This paper describes some recent investigations which have led to the development of a novel deep UV positive tone photoresist system which possesses both high

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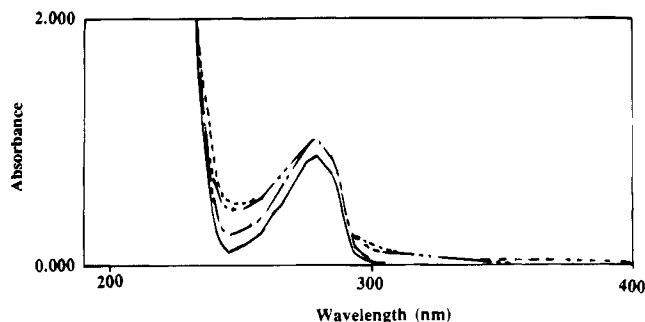

Figure 1. UV absorption spectra of 1 μm thick (—) poly(4-hydroxystyrene-*co*-styrene) (8:2 copolymer); (- - -) copolymer containing 5 wt % (4-(decyloxy)phenyl)diphenylsulfonium hexafluoroantimonate; (- - - -) after UV exposure (···) after postexposure bake at 100 °C for 5 min.

photosensitivity and resolution in combination with excellent reactive ion etch resistance and the ability to be developed in aqueous base.

Experimental Section

Materials and Measurements. The synthesis of *tert*-butyl cholate was prepared as described in a previous article.[11] Poly(4-hydroxystyrene-*co*-styrene) 9:1 and 8:2 copolymers were used as received from the Shin-Etsu Co. The 8:2 copolymer had a M_w = 12 000 g/mol and a M_n = 10 300 g/mol with a polydispersity index of 1.10. Triarylsulfonium salt photoacid generators (4-(decyloxy)phenyl)phenylsulfonium hexafluoroantimonate and (4-(decyloxy)phenyl)phenylsulfonium trifluoromethanesulfonate were synthesized using established methods.[12] Metal-free photoresist devloper MF-312 tetramethylammonium hydroxide was used as purchased from the Shipley Co. UV spectra were recorded on Hitachi U-2000 spectrophotometer.

Deblocking Studies. To 8 parts of poly(4-hydroxystyrene-*co*-styrene), 2 parts of *tert*-butyl cholate, and 0.2 parts of an onium salt photoinitiator was added a sufficient amount of propylene glycol methyl ether acetate to make a 20 wt % solution. Films of this solution were spin-coated onto quartz substrates and then soft baked at 80 °C for 30 min. The photoresist films were exposed to a Hanovia 450 W medium-pressure mercury arc lamp for various times. The course of the deblocking reaction was monitored by recording UV spectra before and after exposure. Specifically changes in the spectrum at the minimum at 255 nm and the maximum at 280 nm were monitored (Figure 1). Next, the substrates were postbaked at 100 °C for 5 min and the UV spectra recorded once again.

Lithographic Evaluation. Photoresist solutions were prepared as described above using various poly(4-hydroxystyrene-*co*-styrene) copolymers and the two different photoacid-generating onium salts. The solutions were filtered through 0.2 μm filters (Scientific Resources Inc.) and then spin coated onto silicon wafers to a thickness of 1 μm using a Headway spin coater. Prior to spin coating, a profile of the thickness versus spin speed was obtained for each photoresist composition. The coated wafers were soft baked at 80 °C for 30 min and then exposed using a GCA Cymer KrF excimer laser stepper at a wavelength of 248 nm with a numerical aperture of 0.45. After a postexposure bake at various temperatures, the photoresist films were developed in a commerical metal-free aqueous base developer (1:1 MF-312:water, Shipley Co.). Reactive ion etching was performed on a Technics Planar Etch II apparatus with CF_4 containing 5% oxygen at a pressure of 350 mTorr and a power of 200 W. The film thickness before and after reactive ion etching was monitored using a Nanometrics Nanospec/AFT.

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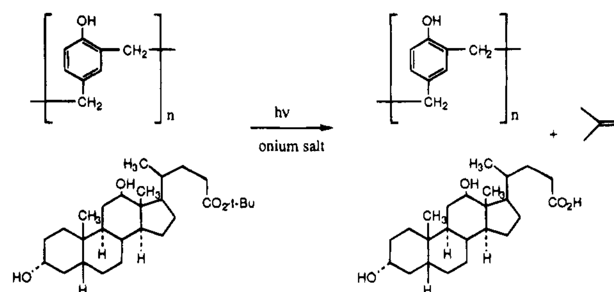
Scheme 1



Results and Discussion

In previous papers, we reported the development of a novel photoresist based on the combined principles of chemical amplification and dissolution inhibition.[11,13] The chemistry of this photoresist is depicted in Scheme 1.

When 15–30% by weight of *tert*-butyl cholate is added to a novolac resin, its solubility in aqueous base is markedly suppressed. If this mixture is imagewise irradiated in the presence of 1–5% of a diaryliodonium or triarylsulfonium salt as a photoacid generator, the *tert*-butyl cholate is catalytically deblocked during the subsequent postexposure bake step to give cholic acid and isobutylene. Cholic acid is very soluble in aqueous base so the exposed regions of the photoresist undergo facile dissolution on development. Similar kinds of photoresists based on *o*-nitrobenzyl cholate ester dissolution inhibitors which do not employ chemical amplification have been developed by researchers at AT&T Bell Laboratories.[14–16]

While this photoresist exhibits very good resolution, contrast, and excellent reactive ion etch resistance, it suffers from two major drawbacks. First, it was found that imaging of photoresist films of moderate thickness (~1.0 μm) led to lower quality images due to the large amount of unbleachable deep UV absorption, especially at 248 nm. As mentioned before, this is inherent in the novolac resins used in the photoresist. Second, the photoresist displays unusual dissolution characteristics which manifest themseleves in that the photoresist switches from positive to negative tone on development depending on the dose. This was traced to a cross-linking reaction which is due to electron-transfer reactions between the cation–radical fragments of the onium salt photoinitiator and the novolac resin followed by coupling of the resulting aromatic free radical species.[17] Despite these problems, it was felt that this chemistry possessed most of the elements required for a high-sensitivity, high-resolution deep UV photoresist and that further investigations should be undertaken to determine whether the problems outlined above could be overcome.

In an effort to circumvent difficulties associated with the initial and unbleachable absorption of novolac resins at 248 nm, it was decided to examine the use of poly-

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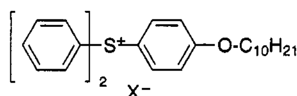
(4-hydroxystyrene) as a base resin. This material is known to have a good transmittance at 248 nm and to be soluble in aqueous base developers. It was discovered, however, that the simple substitution of novolac resins with poly(4-hydroxystyrene) does not lead to workable deep UV photoresists for two reasons: first, due to the very high solubility of this resin, even in very dilute base, a large amount of *tert*-butyl cholate is required to provide sufficient dissolution inhibition in the photoresist. This leads to photoresist compositions with very poor film-forming and spinning characteristics. Second, aqueous base development leads to unacceptable thickness loss even in the unexposed portions of the photoresist.

More recently, copolymers of styrene with 4-hydroxystyrene have become available on an experimental basis from the Shin-Etsu Corp. These copolymers are produced by the anionic copolymerization of styrene with 4-*tert*-butoxystyrene followed by an acid-catalyzed deblocking reaction to give the free phenol-containing copolymer. It was rationalized that these materials should retain the excellent deep UV transmittance characteristics of poly(4-hydroxystyrene) while providing some control over the aqueous base solubility by adjusting the styrene content in the copolymer. Accordingly, preliminary imaging experiments were carried out with two copolymers containing respectively, 4-hydroxystyrene to styrene ratios of 9:1 and 8:2. Similar problems as described previously with poly(4-hydroxystyrene) were encountered with the 9:1 4-hydroxystyrene–styrene copolymer. In contrast, it was found that the 8:2 copolymer was easily dissolution inhibited with *tert*-butyl cholate, yet was readily soluble in commercially available metal ion-free base developers. Furthermore, the high glass transition temperature (T_g = 150 °C) of this copolymer makes it compatible with further resist and device processing steps. For these reasons, it was decided to focus our efforts on this copolymer.

A photoresist composition was prepared consisting of three components. To 80 parts by weight of the 8:2 copolymer was added 20 parts by weight of *tert*-butyl cholate as a dissolution inhibitor. The ratio of these two materials was based on previous novolac optimization studies[6] and on the similarity of the dissolution characteristics of the novolac resins and the 8:2 copolymer. To this mixture was added 2 parts (10% by weight based on *tert*-butyl cholate, 1.96 wt % based on the overall photoresist composition) of either (4-(decyloxy)phenyl)-diphenylsulfonium hexafluoroantimonate or trifluoromethanesulfonate as the onium salt photoacid generators. The structures of these two onium salt photoacid generators are



where X^- = SbF_6^-, $CF_3SO_3^-$

These two onium salts were selected for their excellent solubility in spinning solvents, good compatibility with the poly(4-hydrosystyrene-*co*-styrene) copolymer, and high thermal stability. We also wished to compare the efficiency of the hexafluoroantimonic acid and trifluoromethanesulfonic acids which are respectively produced on photolysis in the deblocking of the *tert*-butyl cholate dissolution inhibitor. Further, these particular sulfonium salts possess excellent absorption at 248 nm (λ_{max} = 262 nm, ϵ = 17 600) as well as a high quantum yields of photolysis (~0.7). Last, the sulfonium salts are easily purified by recrystallization (SbF_6^-, mp 70–72 °C; $CF_3SO_3^-$, mp 67–69 °C) and can be handled under normal laboratory lighting conditions.

Table 1. UV Absorption at 248 nm of a Deep UV Photoresist Film[a]

material	absorbance (transmittance)
copolymer[b]	0.143 (72%)
photoresist[c]	
before exposure	0.268 (54%)
after exposure	0.454 (35%)
after PEB	0.493 (32%)

[a] Film thickness 1 μm. [b] 8:2 poly(4-hydroxystyrene-*co*-styrene) copolymer. [c] Copolymer/*tert*-butyl cholate/onium salt (80:20:2 weight ratio).

Initial experiments were carried out using (4-(decyloxy)phenyl)diphenylsulfonium hexafluoroantimonate as the photoacid generator since it was predicted that the hexafluoroantimonic acid generated would have the highest efficiency in the deblocking reaction. Given in Figure 1 and shown in Table 1 are respectively the UV spectra and the absorbance and transmittance data at 248 nm for the photoresist composition described above before and after exposure using a 450 W Hanovia medium-pressure mercury arc lamp as well as after a postexposure bake of 5 min at 100 °C. These data are compared with those of the original 8:2 4-hydroxystyrene:styrene copolymer. The copolymer resin has excellent transmittance at 248 nm as does the *tert*-butyl cholate (ϵ = 267). Thus, the triarylsulfonium salt is the chief UV-absorbing component of the photoresist which, on addition at a level of 1.96 wt % based on the *tert*-butyl cholate, lowers the transmittance from 72 to 54%.

This photoresist was evaluated under imaging conditions by 248 nm exposure using a KrF excimer laser. Unfortunately, the resist displayed negative tone behavior at several different exposure doses and under various conditions of development. Consideration of the results from the previous work[9] led to the conclusion that cross-linking due to electron transfer from the electron-rich copolymer to the electron-deficient diarylsulfonium cation-radical was taking place with resulting cross-linking of the copolymer. This process is depicted in the following scheme of equations. The intermediacy of the polymeric cations was inferred from studies of model compound studies which showed that aromatic compounds bearing electron releasing substituents gave a high proportion of biphenyl coupling products on irradiation in the presence of onium salt photoinitiators. It is clear that other types of radical reactions may also occur in the polymers including hydrogen abstraction from the benzylic positions and coupling of the resulting free-radical species.

In an effort to avoid or minimize this problem, the concentration of the triarylsulfonium salt photoacid genator was reduced by one-half (5 wt % based on *tert*-butyl cholate, 0.99% based on the photoresist). Since the cross-linking reaction takes place by a stoichiometric process involving coupling of polymeric radical species generated from the radical cationic fragments of the photoinitiator, reducing the photoinitiator concentration

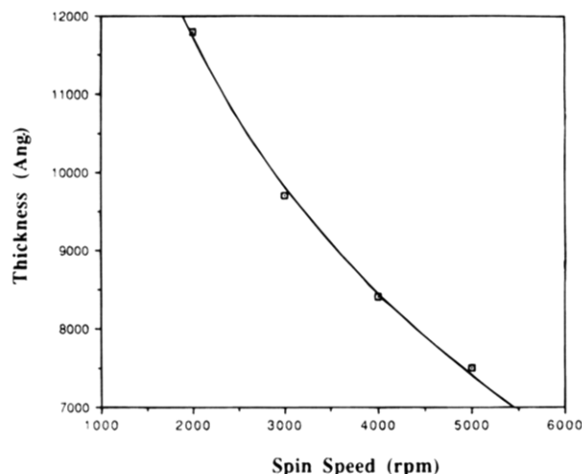


Figure 2. Relationship between the thickness and spinning speed of a 20% solution of 8:2 poly(4-hydroxystyrene-*co*-styrene) copolymer/*tert*-butyl cholate/(4-(decyloxy)phenyl)-diphenylsulfonium hexafluoroantimonate (80:20:5 ratio) in propylene glycol methyl ether acetate.

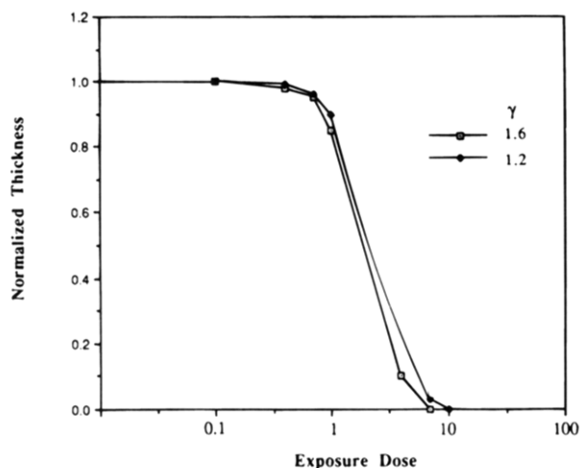


Figure 3. Plots of the normalized thickness versus log dose for the 248 nm exposure of 8:2 poly(4-hydroxystyrene-*co*-styrene) copolymer/*tert*-butyl cholate/(4-(decyloxy)phenyl)-diphenylsulfonium hexafluoroantimonate (80:20:1 ratio) PEB conditions: (□) 140 °C; (♦) 100 °C.

should have a large effect on the efficiency of this cross-linking process. At the same time, the acidolytic deblocking reaction of *tert*-butyl cholate is a catalytic process which should be less effected by a halving of the photoinitiator concentration. The above photoresist could be readily spun onto silicon wafers with controlled thickness as shown in Figure 2. Initial photoresist exposure sensitivity and processing conditions were optimized using the KrF excimer laser. The results are shown in Figure 3. There is a marked effect of the post exposure bake on the sensitivity, contrast and the resolution. However, the highest sensitivity (4 mJ/cm^2) and contrast ($\gamma = 1.6$) was obtained when the exposed to a post exposure bake at 10 min at 100 °C. When the postexposure bake conditions were changed to 1 min at 140 °C, the sensitivity decreased by nearly a factor of 2 (7 mJ/cm^2) while the contrast fell to 1.2. In all cases, the photoresist showed only positive tone behavior and under no conditions was cross-linking observed as with the previous photoresist composition noted leading to negative images. The resolution capabilities of this photoresist are excellent. Figures 4 and 5 show 0.5 μm patterns imaged in a 0.9 μm thick resist.

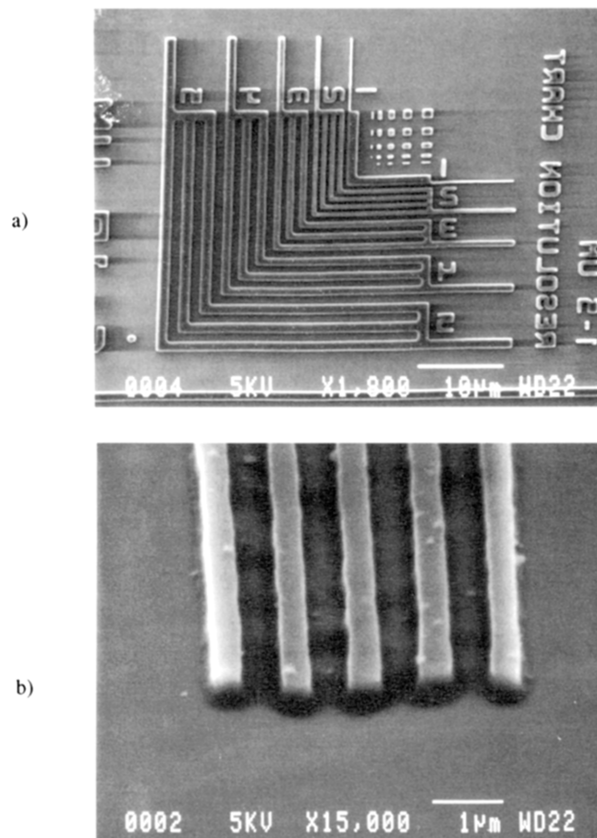


Figure 4. SEM micrographs of (a) 1.2, 1.0, 0.8, 0.5 μm L/S patterns in 0.9 μm thick 8:2 poly(4-hydroxystyrene-*co*-styrene) copolymer/*tert*-butyl cholate/(4-(decyloxy)phenyl)diphenylsulfonium hexafluoroantimonate (80:20:1 ratio); (b) a magnified view of the 0.5 μm L/S pattern.

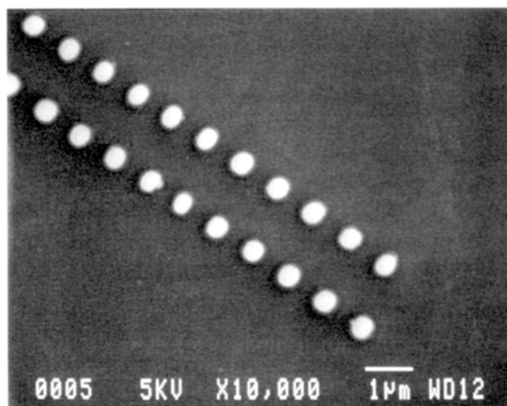
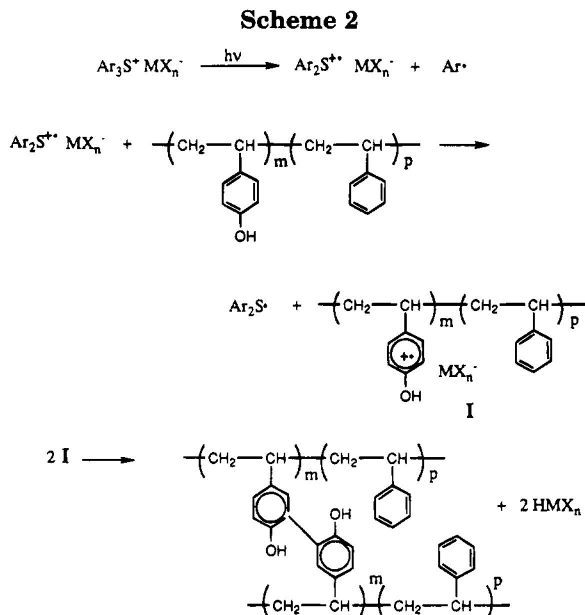


Figure 5. SEM micrographs of 0.5 μm dot patterns in 0.9 μm thick 8:2 poly(4-hydroxystyrene-co-styrene) copolymer/*tert*-butyl cholate/(4-(decyloxy)phenyl)diphenylsulfonium hexafluoroantimonate (80:20:1 ratio).

A similar study was carried out in which (4-(decyloxy)-phenyl)diphenylsulfonium hexafluoroantimonate was replaced with the corresponding trifluoromethanesulfonate salt. It was found that this photoresist was considerably less sensitive than in the former case. A number of different onium salt concentrations and post exposure bake conditions were examined. The best results were obtained with 5 wt % photoinitiator (based on *tert*-butyl cholate) using a 5 min postexposure bake at 140 °C. Under these conditions, the photoresist displayed a sensitivity of approximately 13 mJ/cm^2 with a resolution of 2.0 μm. These results were achieved using undiluted MF-312 (tetramethylammonium hy-

Scheme 2



droxide) developer. There are several possible reasons for the observed decreased photosensitivity of this resist: (1) a poorer catalytic deblocking efficiency of trifluoromethanesulfonic acid, (2) the loss of trifluoromethanesulfonic acid through volatilization, (3) an increased competing crosslinking reaction as per Scheme 2 due to the required higher amount of the triarylsulfonium salt, and (4) a tendency of the acid to diffuse through the resin matrix resulting in line broadening.

While the sensitivity, contrast and resolution of the photoresist composition containing (4-(decyloxy)phenyl)-diphenylsulfonium hexafluoroantimonate as the photoacid generator are acceptable for deep UV applications, it was also important to examine the plasma etch resistance of this material to determine its suitability in downstream circuit fabrication processing steps. Figure 6 gives the results of the study of the etch resistance of this new photoresist with CF_4 containing 5% O_2 as the etchant. An etch rate of 870 Å/min was obtained, indicating that this photoresist exhibits reactive ion etch resistance comparable with currently used novolac-based photoresists.

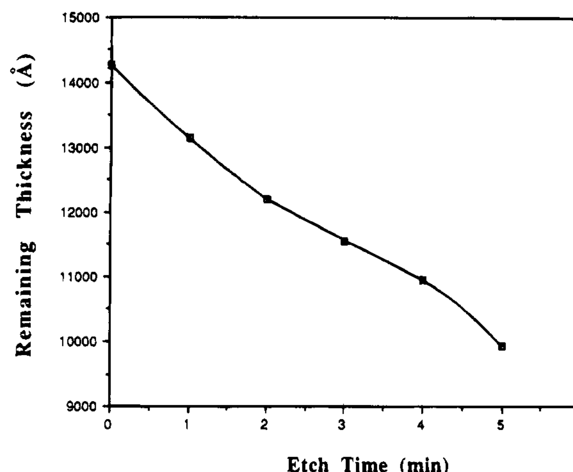


Figure 6. Dry etch resistance of 8:2 poly(4-hydroxystyrene-*co*-styrene) copolymer/*tert*-butyl cholate/(4-(decyloxy)phenyl-diphenylsulfonium hexafluoroantimonate (80:20:1 ratio) using CF_4 containing 5% oxygen at 350 mTorr, 200 W.

Conclusions

Deep UV photoresists which combine the principles of chemical amplification together with dissolution inhibition have been designed which display a combination of a high sensitivity, good contrast and are capable at least 0.5 μm resolution or better. These photoresists make use of 4-hydroxystyrene–styrene copolymers as the base resin and employ *tert*-butyl cholate as the deblockable dissolution inhibitor. The best results were obtained from a photoresist prepared using a 8:2 copolymer with 20 wt % of *tert*-butyl cholate and containing 0.99 wt % of (4-(decyloxy)phenyl)phenyliodonium hexafluoroantimonate as the photoacid generator. It was also observed that the postexposure bake conditions were highly critical in determining the sensitivity and resolution characteristics of the photoresist.

The use of the priniciple of chemically amplified dissolution inhibition described in this article provides a new family of high-sensitivity, high-resolution, and etch-resistant photoresists. The uniqueness of this approach to the design of photoresists is that it allows a greater degree of control over the photolithographic process than usually attained with conventional chemically amplified photoresists. This derives from the fact that each active element of the photoresist, the PAG, the dissolution inhibitor and the polymeric binder can be carefully controlled and optimized separately. When combined, the three elements provide for increased reproducibility in the lithographic process. The results of these process studies will be reported elsewhere.

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