LITHOGRAPHIC FEASIBILITY OF ESCAP BEYOND QUARTER MICRON

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A production-worthy deep UV resist system built on the ESCAP platform is described. The resist consists of a thermally and hydrolytically stable resin and acid generator and thus can be heated at high temperatures for free volume reduction, which provides stabilization toward airborne base contamination. The film densification in conjunction with the use of a bulky acid reduces acid diffusion during postexposure bake, contributing to high lithographic performance. Robust 0.25 µm process latitudes have been demonstrated. Furthermore, the resist has produced excellent 175 nm line/space images with a depth-of-focus of 0.3 μm on a KrF excimer laser stepper with a numerical aperture of 0.60, indicating that the resist allows the use of the current exposure tool in the early 1 Gbit generation.

1. Introduction

The last several years of the deep UV resist development have been primarily devoted to the battle against the airborne base contamination of chemical amplification resists. Although chemically amplified resist systems possess many attractive features such as high sensitivity, high contrast, high resolution, and versatility [1-3], the imaging mechanism based on acid catalysis makes such resists highly susceptible to contamination by airborne basic substances [4]. The contamination results in formation of a skin layer or T-top profile in the positive system and a linewidth shift in negative imaging when exposed resist films are not immediately subjected to postexposure bake (PEB). The most popular engineering solutions to this problem have been (1) use of activated carbon filtration of the enclosing atmosphere [4] and (2) application of a protective overcoat [5-7]. Some additives have been reported to be effective in reducing the PEB delay problem [8-10]. However, full implementation of deep UV lithography in device manufacturing would still require more fundamental built-in stabilization mechanisms. The newer deep UV
positive resist systems currently available on the commercial market are much more environmentally stable due to reduction of either free volume [11-13] or activation energy of deprotection [14,15]. Since the low activation energy systems can suffer from irreproducible synthesis, poor shelf life, linewidth slimming, and serious standing wave patterns on the image side walls, we focused our attention on a thermally and hydrolytically robust, high activation energy system. In addition to the intended stability toward airborne contamination, the robust nature of the ESCAP resist allows manipulation of the bake conditions for optimum performance. Shipley’s UVIIHS and UVIII resists and JSR’s KRF-L, which are available commercially, are built on the ESCAP platform.

This paper describes the design concept and the lithographic performance of the UVIIHS and UVIII resists.

2. Design Concept

Many positive chemical amplification resists are built on a fragile balance of stability; acid-labile protecting groups co-exist with acidic functionalities. Such resist systems cannot be baked above ~130 °C without premature destruction of the protecting groups. In Figure 1 are presented thermogravimetric analysis (TGA) curves of two representative positive resist resins, PHOST partially protected with tetrahydropyranyl and t-butoxycarbonylmethyl groups, to validate the preceding statement. Postapply bake (PAB) at ~100 °C does not completely remove casting

![Figure 1 TGA curves of partially protected PHOSTs](image)
solvents, which are typically hydrogen-bonding with the phenolic polymer [16], or anneal the resist film as the glass transition temperature ($T_g$) of such phenolic polymers are typically $\sim 150\, ^\circ C$ or higher. The large free volume in the resist film results in fast absorption of airborne contaminants and excessive diffusion of photochemically generated acid, jeopardizing lithographic performance. Thus, the key step in the development of the environmentally stable chemical amplification positive resist ESCAP was identification of a robust resist resin [11-13,17,18]. Copolymers of 4-hydroxystyrene (HOST) with $t$-butyl (meth)acrylate (Scheme I) have extraordinary thermal stability with the onset of thermal deprotection observed at $\sim 180\, ^\circ C$ (Figure 2) [11-13,17,18]. To adjust the $T_g$ to $\sim 150\, ^\circ C$, we selected $t$-butyl acrylate (TBA) over the methacrylate as the comonomer in this case. The synthesis of the copolymers has been previously reported [11,17].

Another important issue to consider is selection of an acid generator. An acid generator is present in a resist formulation at a low concentration but plays an extremely important role in lithographic performance. As is the case with the resin selection, the ESCAP resist design demands...
a thermally and hydrolytically stable acid generator because of its high temperature bake processes, which has been described in detail previously [18]. The thermal stability of acid generators varies widely. Figure 3 presents TGA curves of some representative acid generators evaluated in the ESCAP formulation [18]. Triphenylsulfonium salts are exceptionally stable thermally. In contrast, the five-membered imide system begins to evaporate at a temperature as low as 80 °C [18]. Evaporation of an acid generator from the surface of the resist film is another cause of the skin or T-top formation [18]. Since the PAB temperature of the ESCAP resist is high, we selected a bulky and nonvolatile acid generator such as camphorsulfonates. Small acids such as methanesulfonic and commonly employed trifluoromethanesulfonic acids can readily evaporate out of a phenolic resist film [18,19] as shown in Figure 4 [19], which could be yet another reason for generation of the T-top profile. Camphorsulfonic acid exhibits good retention in the phenolic resin film even when baked at 150 °C [19] and thus is a good choice for the ESCAP formulation which requires a high PEB temperature [18]. The PEB temperature must be high enough to minimize standing wave patterns on the resist wall. The weak sulfonic acid can provide good sensitivity in this case because the robustness of the ESCAP resist permits PEB at high temperatures but would not be useful in most other resist systems, which cannot tolerate high temperature PEB.
3. Lithographic Performance of ESCAP (UVIIHS, UVIII)

The robustness of the ESCAP resist design offers several advantages. Ease of the resin synthesis and an excellent shelf life of the resin and the resist are obvious merits while low activation energy systems tend to suffer from some serious problems in these areas. Another obvious merit is the high thermal flow resistance. Since the $T_g$ and thermal deprotection temperature of the ESCAP resin are ~150 and ~180 °C, respectively, the resist image does not exhibit a thermal flow up to ~155 °C, while other chemically amplified positive resists suffer from image distortion at ~130 °C, which is induced by thermal deprotection rather than by thermal flow. The environmental or PEB delay stability of the ESCAP resist is primarily a result of good annealing (free volume reduction) by high temperature bake but also partially due to the incorporation of the acrylate structure (solubility parameter difference) [20]. Figure 5 presents scanning electron micrographs (SEM) of 0.25 µm line/space patterns delineated in the UVIIHS resist, demonstrating no T-top formation or linewidth change up to 7.5 hr of the PEB delay. SEM examinations of delayed images are typically employed to assess the delay stability as is the case with Figure 5. However, resist image profiles are affected by many variables and thus the commonly employed SEM assessment could be misleading, especially when T-top formation is used.
as a criterion for the delay problem. The $^{14}$C labeling technique employed by Hinsberg to study absorption of airborne N-methylpyrrolidone (NMP) in thin polymer films [20], which does not involve lithographic imaging and therefore avoids complication and uncertainty, has unequivocally proved the validity of our annealing concept for environmental stabilization [20,21]. As Figure 6 indicates, the ESCAP resin baked at 100 °C, below its $T_g$, absorbs much less NMP than the APEX resin film due to the acrylate unit incorporated in the structure [20,21]. Furthermore, the ESCAP resin film baked at 170 °C, above its $T_g$, shows NMP uptake further reduced to the level of bare silicon [20,21]. High temperature bake reduces absorption of airborne contaminants due to annealing (reduction of free volume).

Figure 6 NMP uptake kinetics
Standing wave patterns on resist side walls on bare Si must be minimized. Advanced positive resist systems such as UVIIHS and UVIII provide high resolution due to reduction of acid diffusion, which results in formation of strong standing wave patterns on bare Si. This is a formidable problem in the case of the low activation energy resist systems as the standing wave patterns generated cannot be annealed out by PEB. The robustness of the ESCAP resist design permits PEB at a higher temperature (typically by 10 °C) than the already high PAB temperature, which minimizes the standing wave pattern problem. Acid diffusion is necessary to erase standing wave patterns. What is important is to control acid diffusion.

In the ESCAP resist film, the lipophilic t-butyl ester functionality is converted to the hydrophilic carboxylic acid group by exposure and PEB. This change of the ester to carboxylic acid provides much more pronounced dissolution differentiation than deprotection of protected phenol derivatives [22,23]. Figure 7 demonstrates the high developer selectivity (n) of 17 for the UVIIHS resist. The high n value indicates the switching potential of the resist and is a key reason for enhanced contact hole resolution. In comparison, the APEX resist has an n value of ~5. Another interesting aspect of UVIIHS is its high dissolution rate in the exposed regions (R_{max}) of 2100 nm/sec (generation of carboxylic acid, Scheme I) and the high dissolution rate ratio R_{max}/R_{min} (exposed/unexposed) of 10,000. The exposed regions clear very rapidly in an aqueous base developer (0.26 N

\[ \text{Figure 7 UVIII dissolution rate in CD-26} \]

The dissolved remaining resist film can then be easily removed by a simple water rinse. Some data for the resist dissolution selectivity is shown in Table 1 for the CD-26 developer. The dissolution selectivity of 17 is impressive and indicates the potential for high resolution and good contact hole filling. To achieve the best results, it is important to control the PEB temperature, as shown in Figure 8. The PEB temperature must be kept below 90 °C to ensure that acid diffusion is minimized, which in turn reduces the standing wave pattern problem.

tetramethylammonium hydroxide in this case). The conversion of the TBA unit to the acrylic acid (AA) unit in the ESCAP resin and resist films (Scheme I) can be readily monitored by IR spectroscopy. Figure 8 presents IR spectra of poly(HOST-co-TBA) and poly(HOST-co-AA) authentically prepared by acidolysis of the former in solution. Since the free and hydrogen-bonded ester groups of the ESCAP copolymer are converted to a carboxylic acid by acid-catalyzed thermolysis in the resist film, it is not easy to follow the reaction by looking at the 1700 cm\(^{-1}\) carbonyl region. Therefore, we monitor the reaction using the IR peak at 1150 cm\(^{-1}\) (or 1360 cm\(^{-1}\)), which shrinks as the t-butyl ester is converted to carboxylic acid (Figure 8). The chemical contrast curve of the ESCAP resist as studied by IR spectroscopy is shown in Figure 9 along with the thickness loss in the exposed regions that occurs upon PEB (150 °C in this case) due to liberation of isobutene. This shrinkage in the exposed areas is also a good measure of the degree of conversion [22,23]. Both the IR and thickness changes indicate that the deprotection reaction is completed at \( \sim 15 \text{ mJ/cm}^2 \) when PAB and PEB are 150 °C (60 and 90 sec, respectively, in this experiment). The lithographic contrast curve of the resist is also presented in Figure 9, measuring

![IR spectra of poly(HOST-co-TBA) and poly(HOST-co-AA)](image)

**Figure 8 IR spectra of poly(HOST-co-TBA) and poly(HOST-co-AA) film**

the thickness in the exposed regions after development with CD-26 (0.26 N tetramethylammonium hydroxide aqueous solution) for 60 sec. It is clear that the conversion of the t-butyl ester to carboxylic acid at the clearing dose of 6 mJ/cm\(^2\) is much smaller than 100 % according to the IR
and thickness changes. Our inverse-gated $^{13}$C NMR studies of the exposed/postbaked resist film indicated that 60% of the $t$-butyl ester was converted to carboxylic acid at the clearing dose of 6 mJ/cm$^2$.

Figure 10 presents linewidth changes as a function of the exposure dose and the PEB temperature for nested 0.25 µm features of UVIIHS printed on a Micrascan (MS) II with a numerical aperture (NA) of 0.50. The PAB temperature was 130 °C for 60 sec. The linewidth shift per °C of the PEB temperature is ~8 nm/°C at the PAB temperature of 130 °C. The APEX-E resist exhibits a linewidth change of 15 nm/°C. The shift of UVIIHS appears to decrease with increasing PEB temperature; 10.2±2.3 nm/°C for the PEB temperature range of 130-135 °C and 6.1±1.2 nm/°C for the 135-140 °C PEB temperature range. At higher PAB temperatures, the linewidth sensitivity of UVIIHS to the PEB temperature variation is reduced to ~4 nm/°C. This is consistent with better annealing at higher PAB temperatures. It is quite significant that a resist based on high activation energy deprotection can achieve such small dependency of the linewidth shift on the PEB temperature variation, smaller than one might predict solely on the basis of the chemical kinetics of deprotection. This result indicates that at higher PEB temperatures (> 135 °C) the deprotection reaction is not reaction-controlled but diffusion-controlled [24].
Figure 11 shows linear resolution, and exposure latitude and depth-of-focus (DOF) for 0.25 µm features of UVIHS on bare Si imaged on a Micrascan II (0.50 NA). The resist had a linear resolution down to 0.225 µm and cleanly resolved 0.200 µm line/space patterns at 10%.

Figure 10 Linewidth change vs. dose and PEB temperature for 0.25 µm nested images of UVIHS on MSII

Figure 11a Linear resolution of UVIHS on MSII
overexposure of the 0.250 µm features. The bias between the isolated and dense 0.300 µm features was ~+30 nm. The exposure latitude and the DOF for the dense 0.25 µm patterns were 17% and 1.2 µm, respectively. All these performance parameters are greater than those of APEX-E. The isolated 0.25 µm lines showed a slightly smaller DOF of ~1.0 µm with a lower exposure latitude of ~13%. Further optimization of isolated line performance is underway.

Although positive resists are more suited for contact hole patterning, the contact level typically provides the least resolution and process latitude. The UVIIHS and UVIII resists have a remarkable underexposure latitude and can open 0.20 µm contact holes. UVIII demonstrated the dose latitude of ~20% and DOF of ~1.2 µm for 0.30 µm contact holes on a Micrascan II (NA 0.50). Figure 12 shows DOF of 0.30 µm contact holes printed in UVIII on a Micrascan II.

Figure 11b Exposure latitude of UVIIHS on MSII  Figure 11c DOF of UVIIHS on MSII

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Figure 12 Contact hole imaging (0.30 µm) of UVIII on MSII (0.50 NA)
In addition to the airborne contamination, chemical amplification resists are sensitive to substrate surfaces in general; nitride substrates such as titanium nitride give resist image profiles characterized with 'foot' in the case of positive systems. The ESCAP resist has been shown to be
less susceptible to this problem than APEX [13,17]. In Figure 13 are compared 0.35-0.20 µm line/space patterns delineated in APEX and UVIIHS on TiN using a Micrascan II (0.50 NA). The APEX resist exhibits significant footing whereas UVIIHS has little or no foot. The UVIIHS resist achieved 0.20 µm resolution on TiN at NA of 0.50 (Micrascan II) as Figure 13 demonstrates.

The UVIIHS and UVIII resists have an excellent resolution capability with a k factor of 0.4 and are thus capable of achieving 1 Gbit geometries when imaged on a high NA exposure tool. Figure 14 shows the linear resolution down to 0.20 µm obtained with UVIIHS at 16 mJ/cm² on a 0.60 NA Nikon S201A. As Figure 15 demonstrates, performance on this 0.60 NA stepper has defined the process capability at 0.175 µm resolution. The 0.175 µm line/space patterns were nicely delineated with DOF of 0.3 µm at a slightly higher dose of 17 mJ/cm².

Figure 14 Linear resolution of UVIIHS on Nikon S201A (0.60 NA)

Figure 15 High resolution imaging of UVIIHS on Nikon S201A (0.60 NA)
4. Summary

The robustness of the ESCAP resist design has resulted in commercialization of high performance, environmentally stable UVIHHS and UVIII resists. The free volume reduction has proved to be a viable concept for producing stable, production-worthy images for 256 Mbit DRAM and other logic device manufacturing. Improvements in the acid generator, processing conditions, and overall formulation, coupled with high NA exposure tools, resulted in 0.20 µm linear resolution with excellent PEB delay stability. Reduction of footing on nitride substrates has been realized. Resolution of 0.175 µm with a small but significant DOF has been demonstrated, which suggests that high NA 248 nm exposure systems could be used for early learning of 1 Gbit DRAM and related logic products.

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References


