A New Environmentally Stable Protective Group for Deep UV Resists: Methoxy(tetrahydropyranyl) Ether

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ABSTRACT: Deep UV photoresists are designed to be used in the manufacturing of highly integrated chips (>16 Mbit). They differ from the conventional photoresists in their principal chemistry. The vast majority of positive deep UV resists are based on protected poly(hydroxystyrene) resins and photochemical acid generators (PAG). They rely on photochemically induced acid-catalyzed reactions (chemical amplification) to generate the desired pattern and meet the high-sensitivity requirements. It turned out that the type of the acid labile protective group is of paramount importance for the performance of the resists. It has to be stable enough not to be cleaved by the weakly acidic phenol at room temperature, but has to be labile enough to be cleaved readily even at the top of the resist where portions of the generated acid may be neutralized by airborne bases. Selection criteria for useful groups and the performance of the very well suited protective group methoxy(tetrahydropyran) are described in this paper. © 2000 John Wiley & Sons, Inc. J Appl Polym Sci 78: 208–216, 2000

Key words: DUV photoresists; new ketal-type protective group; delay stability

INTRODUCTION

The vast majority of positive deep UV resists are based on protected poly(hydroxystyrene) resins and photochemical acid generators (PAG). They rely on photochemically induced acid-catalyzed reactions (chemical amplification) to generate the desired pattern and meet the high-sensitivity requirements. It turned out that the type of the acid labile protective group is of paramount importance for the performance of the resists. It has to be stable enough not to be cleaved by the weakly acidic phenol at room temperature, but has to be labile enough to be cleaved readily even at the top of the resist where portions of the generated acid may be neutralized by airborne bases. Selection criteria for useful groups are given. Upon deprotection, ketal-type protective groups form stable ketones which do not undergo any further side reactions in contrast to acetal-type groups. Compared to other ketal groups, the thermal and storage stability is higher. Evaluation of the resist performance of the very well suited methoxy(tetrahydropyranyl) protective group revealed high sensitivity, large delay stability, and high resolution.

Almost all electronic companies consider deep UV (DUV) lithography at least for backup versions of 64 Mbit DRAM's and as the prime candidate for quarter-micron lithography to produce 256 Mbit DRAM. The hesitant switching over to DUV lithography is due to the only recent development of production worthy equipment (stepper, track, photosector integration) and materials (DUV photoresists). The change of resist chemistry from the novolac/naphthoquinone resists to chemical amplification systems has been described recently.[1] The chemical amplification systems rely on acid-catalyzed photoreactions to meet the sensitivity requirements in conjunction with the low-exposure fluxes delivered by DUV exposure systems. These systems have to be designed so that they can be used in a

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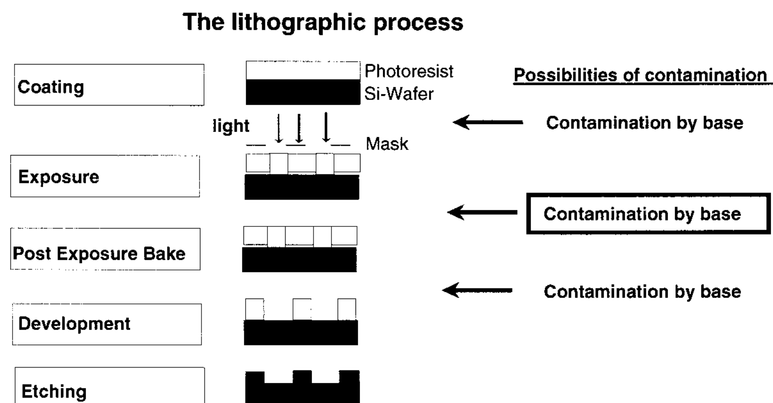
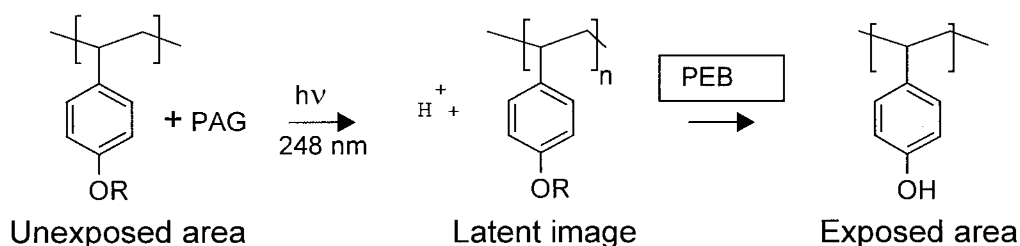


Scheme 1 The lithographic process: Indication of contamination possibilities.

production environment as easily as conventional novolac systems. The lithographic processing differs from that of novolac resists only in the postexposure bake (PEB) step. Although this step is used occasionally in conventional processing to reduce standing-wave effects, postexposure baking (PEB) is absolutely necessary in almost all chemical amplification DUV resists to initiate deprotection. In the PEB step, the latent image of photochemically produced acid is converted to the corresponding alkaline soluble area, which is afterwards removed in the development step.



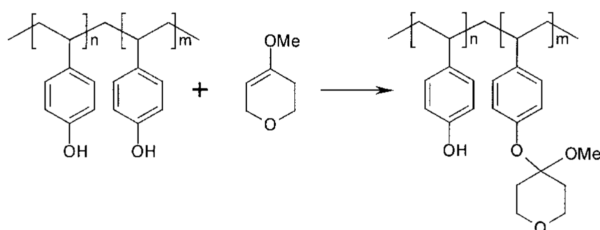
The key factor to good resist performance is the stability of the exposed image until it is developed. The resist image is especially sensitive to basic contaminations during processing delay times. The possibilities of airborne contaminations during the lithographic process are manifold and depicted in **Scheme 1.**

EXPERIMENTAL

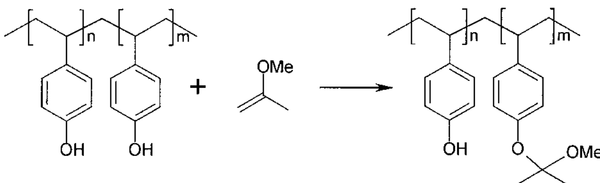
Materials

Poly-(*p*-hydroxystyrene) (PHS) resins were synthesized in-house or Lyncure PHM-C resin (Maruzen Petrochemical, Japan) was used. 4-Methoxy-5,6-dihydro-2H-pyran was purchased from Aldrich.

Synthesis of Partly Substituted Poly(hydroxystyrene) by Methoxy(tetrahydropyran) (MOET-PHS). Poly(*p*-hydroxystyrene) (48 g, 0.4 mol; M_n: 4000 g/mol) is dissolved in 200 mL tetrahydrofurane, 4-methoxy-5,6-dihydro-2H-pyran (39.4 g, 0.31 mol), and 0.5 g sulfuric acid were added and the reaction mixture was stirred at room temperature for 12 h. A solution of tetramethyl ammonium hydroxide was then added to neutralize the acid and the resulting polymer was precipitated in water, filtered, and dried in air. The yield was 61 g (91%). Protective group content was 44 mol % (by ^{1}H-NMR).



*Synthesis of Partly Substituted Poly(*p*-hydroxystyrene) by Methoxypropene (MP-PHS).* According to the procedure described above, a polymer of PHS partly substituted with methoxypropene (50 mol %) was synthesized.



Further characterization of the polymers was done with thermogravimetric analysis (TGA).

The TGA data (Fig. 1) revealed that the thermal stabilities of the two synthesized materials are different. The MOET-substituted PHS is stable up to an onset temperature of 150°C, whereas the MP-substituted PHS is less stable, starting decomposition at an onset temperature of 120°C. The TGA data are also used to calculate the protective group content besides ^{1}H-NMR spectroscopy.

Equipment

Exposures were done either with an ASM-L Excimer stepper 5500/70 or 5500/90 with 0.5 NA coupled with a Lambda–Physik laser (248 nm). The experiments were performed on Si wafers coated with a bottom antireflective coating.

Time to clear measurements were done with a Perkin–Elmer development rate monitor (DRM). TGA measurements were done with a Perkin–Elmer TGA 7.

RESULTS AND DISCUSSION

Resist Chemistry

The invention of acid-catalyzed deprotection chemistry dates back to 1973 (Smith of 3M Company used tetrahydropyranyl-protected novolacs and trichloromethyl-triazines as photoacid generators[1]). However, the breakthrough was not achieved until the pioneering work of Frechet and Willson, who introduced this principle into photolithography and termed it chemical amplification. They used the thermally stable, acid-labile *t*-butoxycarbonyl group to protect PHS resins in conjunction with sulfonium or iodonium salt photoinitiators. Upon irradiation, the salts liberate an acid that, upon subsequent baking, catalyzes cleavage of the protecting group to restore the PHS resin. These photoresists are extremely fast and exhibit high contrasts; however, an inherent disadvantage is their sensitivity to basic contaminations.[2]

Depending on the delay time between exposure and postexposure bake, airborne basic contaminations can cause resist profiles that look T-shaped instead of rectangular and incomplete development with bridging of the pattern. Furthermore, acid diffusion and acid quenching may lead to acid gradients and consequently to resist images that are different at various delay times. To solve this delay time problem, the chemistry and process conditions have to be optimized to guarantee an image stability. The formation of T-tops during delay times between exposure (generation of acid) and postexposure bake (acid-catalyzed decomposition of the dissolution inhibitor) was first reported for *t*-butylcarbonate (*t*-BOC)-containing resists. Measures to prevent such T-tops are either to process in filtered air,[3] to use an acidic top coat layer,[4] or annealing the polymer to densify the film to reduce free volume in the resist. Contrary to these physical measures, we determined the type of the protective group to be of paramount importance for this behavior. Several of such protective groups, *t*-butyl carbonates,[5] *t*-butyl ether,[6] tetrahydropyranyl,[7] or silyl ether[8] are well-known in resist chemistry. By looking to the reported hydrolysis data of different acid labile protective groups (Table I),[9] it is apparent that the carbonates are most stable against acid-catalyzed hydrolysis and need the highest proton concentration (lowest pH). The data in Table I, derived in aqueous solution, may not be directly transferable to the chemistry in the resist layer. Nevertheless, conclusions may be drawn. If basic airborne contaminations neutralize parts of the photogenerated acid in the top layer, an acid-cleavable group should be chosen that is readily cleaved at relatively high pH values. Consequently, a small acid concentration should be sufficient for the cleavage. However, the protective group must be so stable that the slightly acidic phenol of the polymer (pKa 10) does not decompose the inhibitor under process conditions (soft-

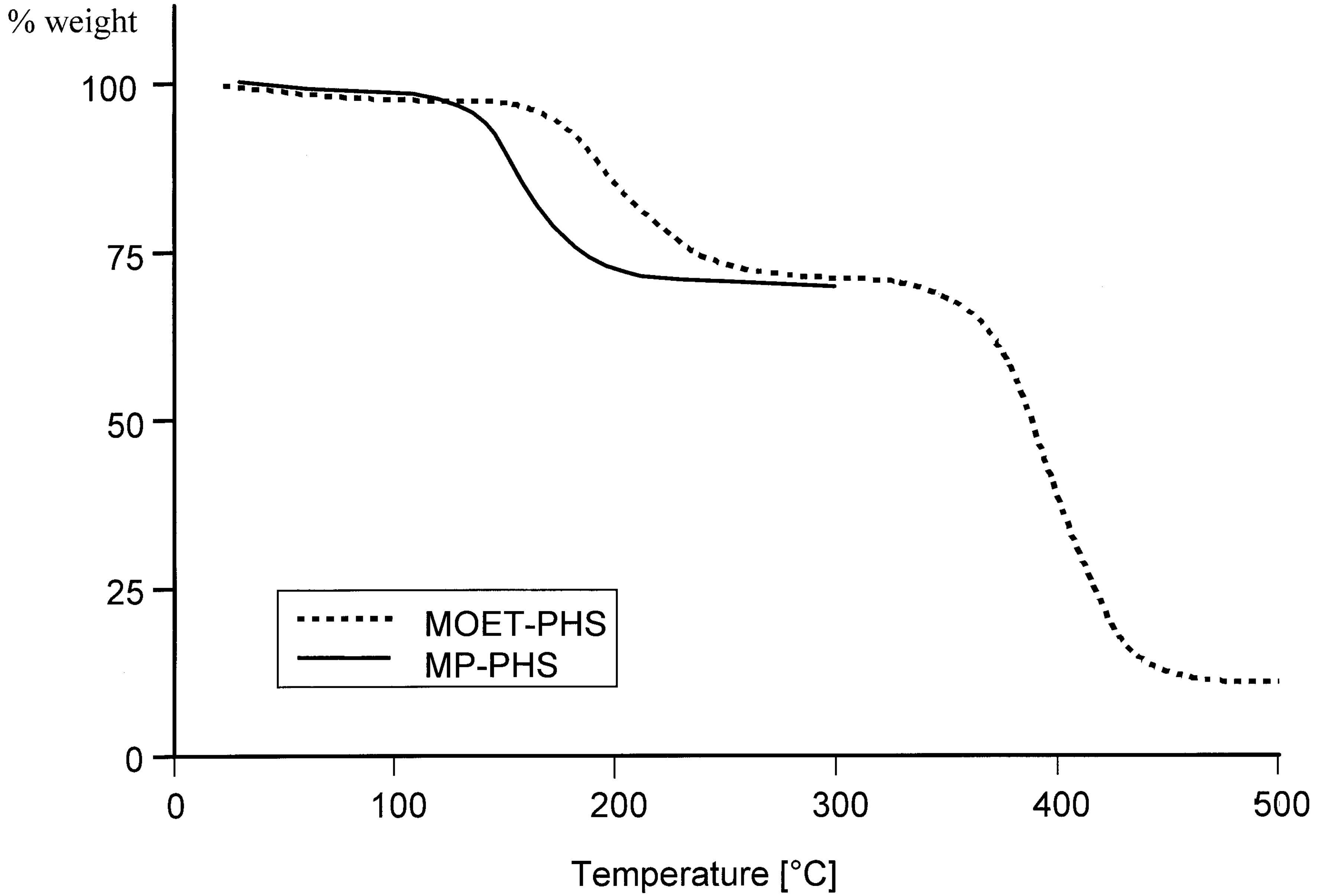


Figure 1 TGA diagrams of 44 mol % MOET-PHS and 50 mol % MP-PHS.

Table I Reactivity of Several Protective Groups Against Hydrolysis in Aqueous Solution

		pH 1	pH 2–4	pH 4–6
Protection of the hydroxyl group: Esters				
—O—CO—C$(CH_3)_3$	Pivaloate esters	L	L	L
—O—CO—Ph	Benzoate esters	L	L	L
—O—CO—Bz	Benzylcarbonate	L	L	L
—O—CO—H	Formate ester	H	M	L
Protection of the hydroxyl group: Ethers				
—O—CH_3	Methylether	L	L	L
—O—C$(CH_3)_3$	t-Butylether	L	L	L
—O—THTP	Tetrahydrothiopyranylether	H	H	L
—O—THP	Tetrahydropyranylether	H	H	M
—O—MOET	Methoxytetrahydropyranylether	H	H	M
—O—C$(CH_3)_2(OCH_3)$	1-Methyl-1-methoxyethylether	H	H	M
—O—THF	Tetrahydrofuranylether	H	H	H
—O—Si $(CH_3)_3$	Trimethylsilylether	H	H	H
Protection of the phenolic group:				
—O—CH_2—Ph	Benzylether	L	L	L
—O—CO—O CH_2—Ph	Benzylcarbonat	M	L	L
—O—C$(CH_3)_3$	t-Butylether	H	L	L
—O—CH_2—O CH_3	Methoxymethylether	H	M	L
—O—Si—(t—Bu) $(CH_3)_2$	t-Butyl-dimethylsilyl	H	H	M

H = high, M = marginal, L = low reactivity at the pH value specified.

bake/postexposure-bake). Thus, the groups considered are those with high reactivity at low pH values and marginal reactivity at slightly acidic pH values.[4–6]

As depicted in Table I, only limited data are available from protection of the phenolic group. Thus, the data of the protection of the hydroxyl group were used to select specific protective groups. Because silylethers are not desirable in conventional resists, the tetrahydropyranyl, methoxy(tetrahydropyranyl), and 1-methyl-1-methoxyethyl (methoxypropen) groups seem to be the most promising protective groups. A differentiation between these groups can also be calculated from literature data.[10] The relative hydrolysis rates of these acetal/ketal systems are shown in Table II.

Table II Relative Hydrolysis Rates

	THP	MOET	MOCH	MP
k_{rel}	1	3	8	20

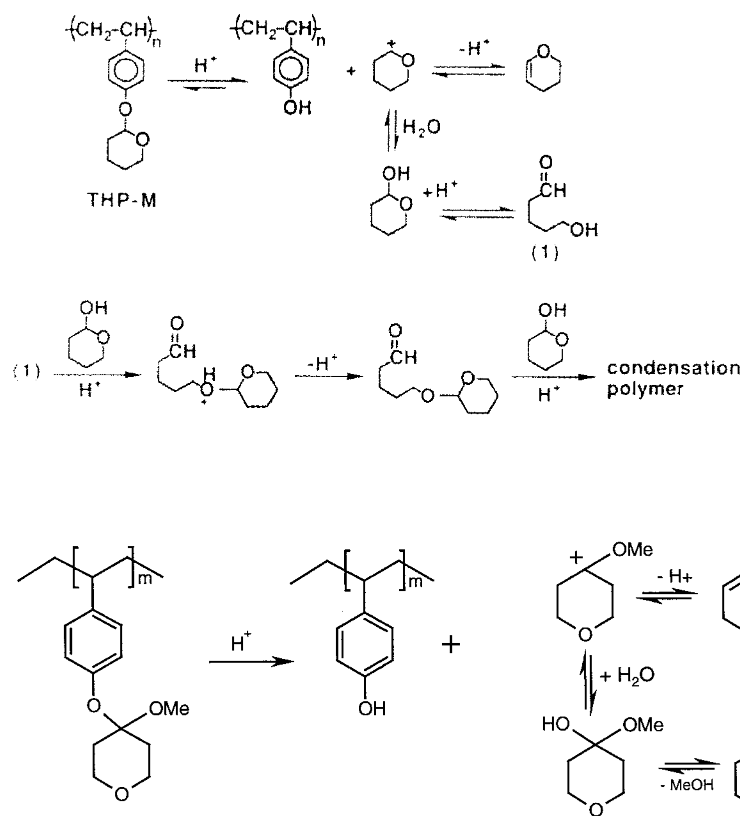
The tetrahydropyran (THP) group has been investigated in detail in the literature. It has been demonstrated that the THP group is insensitive to basic contaminations; however, it appears that THP-protected resists have some disadvantages due to consecutive reactions of the cleavage product which reduce the developability.[11] These reactions are possible because the acetal group gives rise to the formation of aldehydes which are prone to further condensation reactions (Scheme 2).

Resist Performance of Ketal-Type Resists

We have evaluated acetal- and ketal-type protective groups since the beginning of the 1990s.[12] Most recent publications have described ketal chemistry and compared acetal to ketal chemistry.[13,14] According to Table II and Scheme 2, the ketal-type protecting groups should be more easily cleaved compared to THP and should not yield any further side products due to the formation of inert ketones. Due to the lower thermal stability found with the resins based on the methoxypropene-protective group, the evaluations were concentrated on the MOET group-based resists.

Photoacid Generators

Evaluation of photoacid generators showed that different types are useful. All photoacid genera-



Scheme 2 Acid-catalyzed deprotection and consecutive side reactions.

tors tested showed a reasonable sensitivity at a loading of 4 wt % (Fig. 2). The resist layer thickness was 1 μm. The developer was a diluted standard tetramethyl ammonium hydroxide (TMAH) developer at a concentration of 2.34% TMAH, diluted with water in the ratio of 10 : 4. The SUCCESS-type initiators were described previously.[15]

Delay Behavior

The sensitivity and contrast can be determined with the contrast curve, depicting the layer thickness as a function of UV dose after development of the resist. The contrast curves of a resist based on PHS with 44 mol % of the MOET-protecting group showed high sensitivity (<10 mJ/cm^2), high contrast, and no deviation within 2-h delay between exposure and postexposure bake, thus demonstrating excellent processibility (Fig. 3).

In another experiment, we compared the delay behavior of such a resist by storing one exposed wafer in a normal contaminated clean-room atmosphere and the other in a nitrogen chamber for 2 h. A third wafer was processed immediately after exposure. The contrast curves of all three wafers were identical.

Two hours of delay is enough to enable such a resist to be processed in a commercial chip production line. We looked at the delay behavior even for a much longer time (Fig. 4). Within 24-h delay time, the resist was processible without showing any T-tops or dissolution inhibition and the time to clear only changed within a $\pm$10% range.

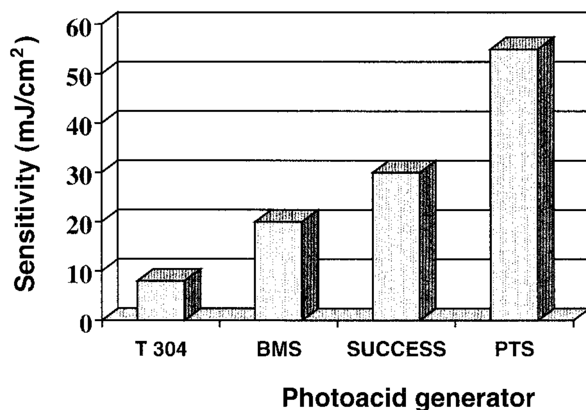
Linearity

The MOET-protected resist showed an excellent linearity down to 0.25-μm pattern (smallest pattern on the mask; Fig. 5). This figure also demonstrates the resolution capability.

Pattern Generation

Contrast curves are an indication of the delay behavior, but the ultimate proof are the actual pattern sizes.

Linewidth changes during delay times are believed to be due to acid diffusion. The driving force of diffusion, the acid gradient within exposed and unexposed areas, is reduced if only small amounts of acid are used to decompose the inhibitor. Thus, the use of such a labile group is also favored in



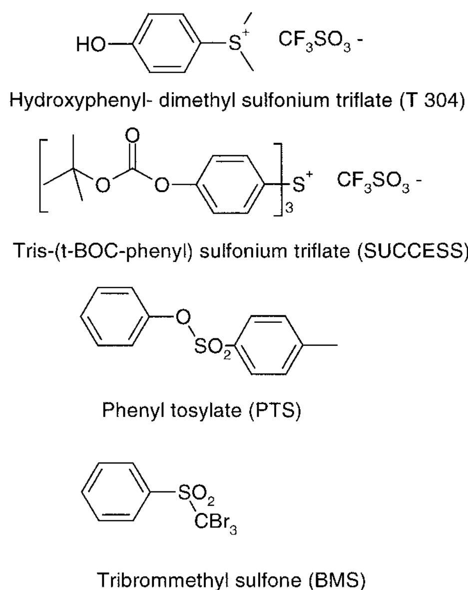
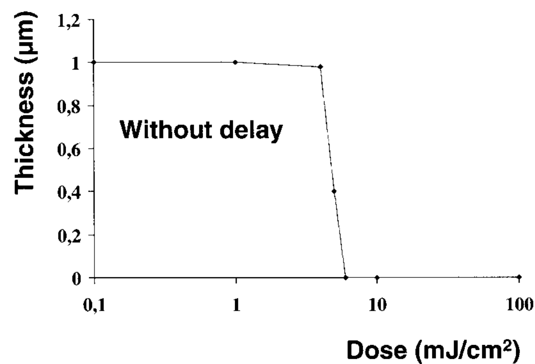


Figure 2 Sensitivity of MOET-PHS resist as a function of photo acid generator type.

terms of linewidth stability. REM pictures of a 0.4-μm pattern of a MOET resist, processed with a soft-bake of 60 s/90°C, exposed with 3.95 mJ/cm^2 postexposure backed for 60 s/70°C, and developed with a special TMAH-based developer for 60 s exhibit no linewidth changes within 30-min delay (Fig. 6).

Summary and Conclusion

DUV photoresists rely on photochemically induced acid-catalyzed deprotection (chemical amplification) of partially protected poly(hydroxystyrene) resins to generate the desired pattern and meet the high-sensitivity requirements. It turned out that the type of the acid labile protective group is of paramount importance for the performance of the resists. It has



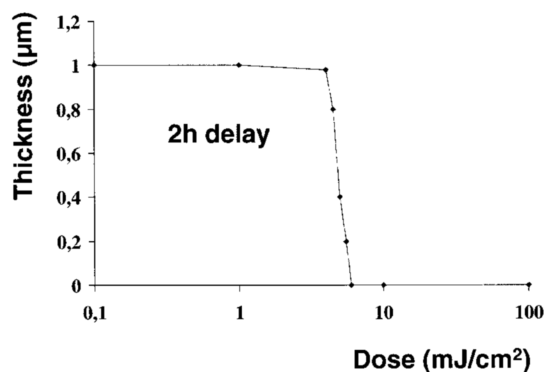


Figure 3 Contrast curves of MOET-protected resist without and at 2-h delay.

to be stable enough not to be cleaved by the weakly acidic phenol at room temperature, but has to be labile enough to be cleaved readily even at the top of the resist, where portions of the generated acid may be neutralized by airborne bases. Selection criteria based on deprotection rate and absence of side reactions resulted in the use of methoxy(tetrahydropyran) as a very well suited protective group.[16] Although acetal-protected resists generate alde-

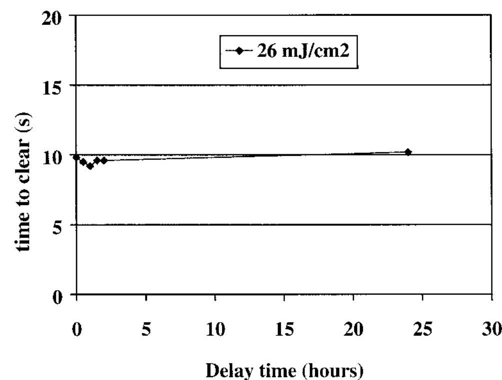


Figure 4 Delay behavior of MOET resist up to 24 h (time to clear monitoring).

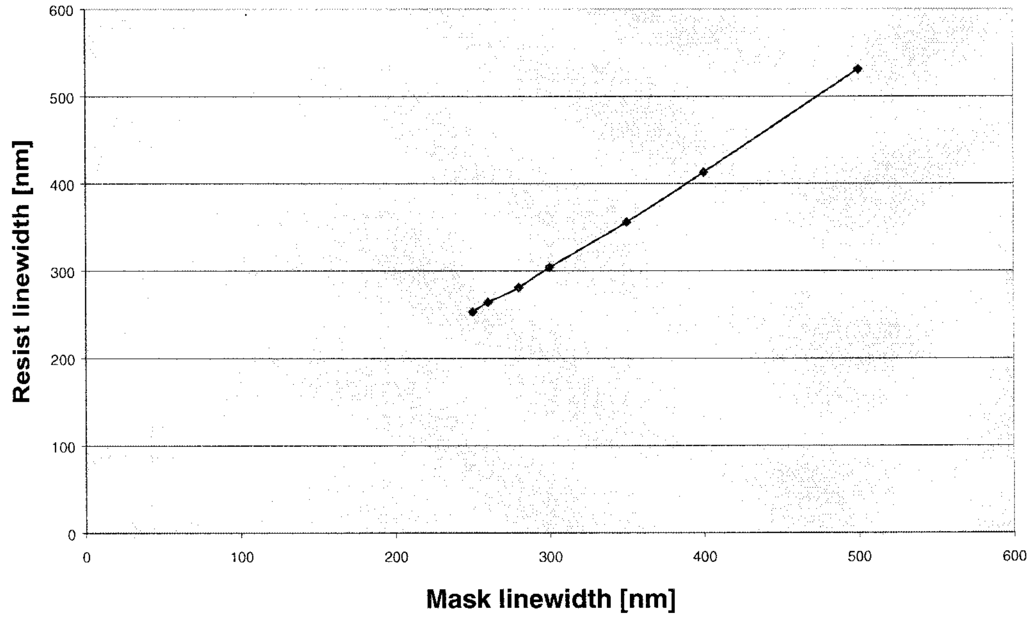
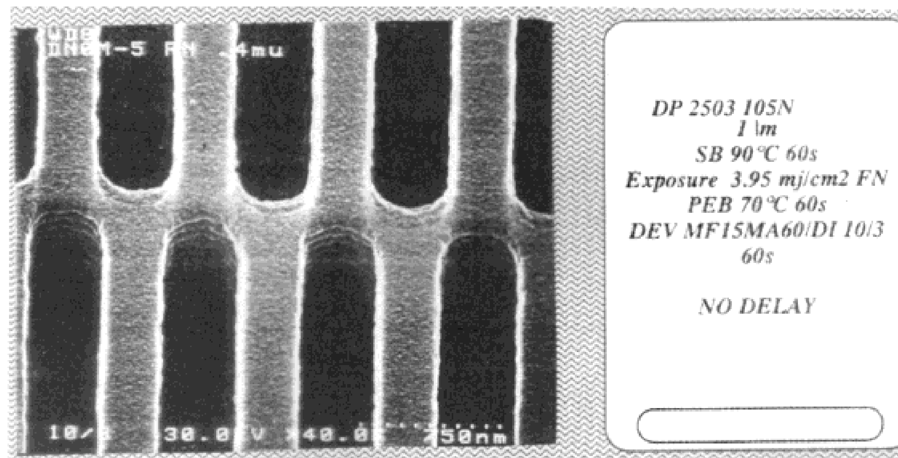


Figure 5 Linearity of MOET protected resist.



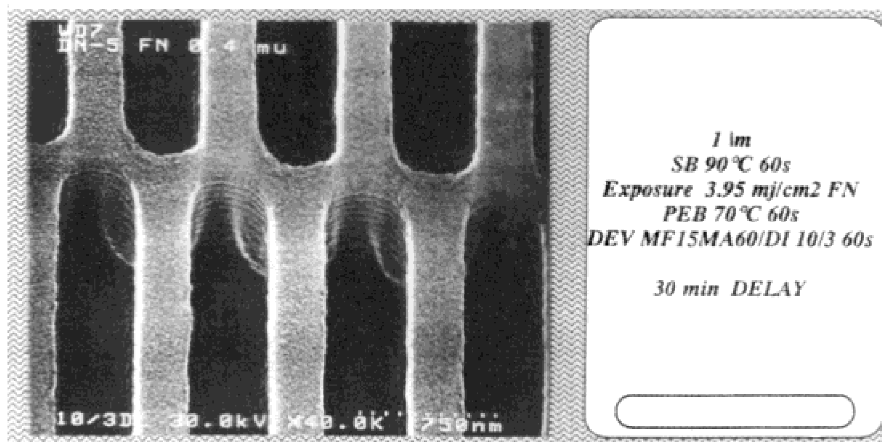


Figure 6 Linewidth control of MOET resist within 30-min delay time.

hyde cleavage products which are prone to undesirable side reactions, the MOET group results in the formation of a ketone which does not undergo any further reactions in the resist. Compared to the methoxypropene ketal group, MOET is deprotected slower by a factor of 7. The lithographic sensitivity obtained with MOET, however, is high enough (<10 mJ/cm^2) to be used in practical resists and the lower deprotection rate results in higher storage stability. Resists based on MOET-protected resins are very sensitive, showed almost no delay behavior, and yielded good resolution.

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