

Critical Process Parameters of an Acetal Based Deep UV Photoresist

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The present paper gives a first introduction into the resist scheme and the chemistry of a newly developed acetal-based, positive tone deep UV photoresist, called RS 1594/E. The material consists of a phenolic polymer, a dissolution inhibitor, and a photoactive compound. The dissolution inhibition of the polymer is achieved using a poly-*N,O*-acetal, which undergoes an efficient acid catalyzed bond cleavage. The radiation induced catalytic reaction starts at ambient temperatures and the latent image stabilizes in a dark reaction. The process is completed by the application of a post exposure bake resulting in the formation of highly soluble dissolution promoting fragments, namely aldehyde and alcohol derivatives. The properties of the main resist components have been studied in detail and their influence on the lithographic performance will be discussed. In addition, new critical process parameters have been identified and their impact on the lithographic performance of RS 1594/E was analyzed. The dissolution rate ratio between exposed and unexposed resist areas, the post exposure bake temperature, and the delay time between exposure and post exposure bake were determined as the most significant parameters and will be discussed in more detail. Prolonged intervals are found to be mainly responsible for the increased formation of an insoluble surface inhibition layer ("T-topping") and a significant linewidth decrease.

Compared to state-of-the-art materials, RS 1594/E shows a noticeable improvement in delay time behavior. Even after 60 minutes delay between exposure and PEB acceptable results may be achieved without any formation of "T-shaped" profiles, and a nearly constant linewidth. The surface inhibition effect is markedly reduced by the use of certain organic additives and an optimized photoacid generator. SEM pictures of 0.24 μm , 0.26 μm , and 0.28 μm line and space patterns demonstrate the excellent resolution capability of RS 1594/E.

1. Introduction

The increasing demands of microelectronic device manufacturing require a change from conventional near UV optical lithography using inhibition type diazo naphthoquinone/novolak systems to novel irradiation technologies and photoresist materials. Deep UV lithography is among the most promising technologies to fulfill the requirements of semiconductor industry for ULSI device fabrication with a minimum resolution of at least 0.35 μm [1]. Among the many resist schemes suggested for this technology, positive tone materials based on the principle of chemical amplification were steadily improved during the last few years. The inherent advantages of chemically amplified resists, such as high photospeed and excellent ultimate resolution were found to be sensitive to new critical process parameters which

have to be carefully considered. It turned out that certain delay times between the applied process steps are very critical to resist performance. One of the most interesting and difficult to solve aspect is the formation of a surface inhibition layer, which results in "bridged" sub-half micron patterns or "T-shaped" profiles. These problems were mainly responsible for the delayed availability of positive tone deep UV photoresists to the market.

The critical dimensions of recently developed positive tone deep UV photoresists are significantly less affected by extended intervals. The acetal-based photoresist RS 1594/E is one example of this new generation of deep-UV resists offering excellent resolution and adequate process stability.

2. Chemical Amplification in Acetal-Based Deep UV Photoresists

The benefits of acid sensitive compounds for use in re-prographics [2] were first recognized by researchers at 3M, and soon led to their adaption to microlithography. The creation of the term "chemical amplification" by Itoh and Willson [3] was the startup for a new and promising technology for microlithographic systems as documented by the many concepts, which were investigated within the last few years [4-6]. At present several positive tone deep-UV resists have achieved a precommercial stage. RS 1594/E, an acetal containing deep UV photoresist developed by Hoechst, is also based on the chemistry of chemical amplification and shows a complete specialization of the individual resist components (Figure 1).

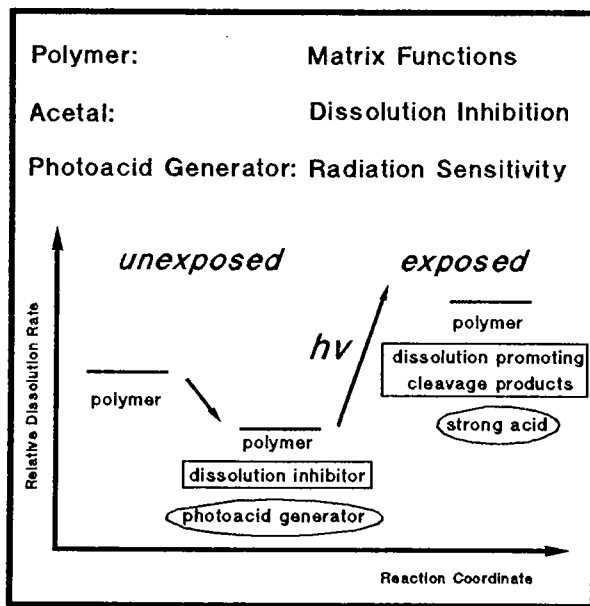


Fig. 1: Complete specialization and dissolution rate scheme in RS 1594/E

The three component approach offers a significant advantage over other resist schemes, as every component may be optimized according to its specific task. The film forming phenolic polymer fulfills the matrix functions, the polymeric acetal acts as a dissolution inhibitor/promoter and the photoacid generating compound (PAC) is responsible for radiation sensitivity. Upon deep UV irradiation the PAC produces a strong acid, which induces an efficient bond cleavage of the acetal (Figure 2). The cleavage products (alcohols and

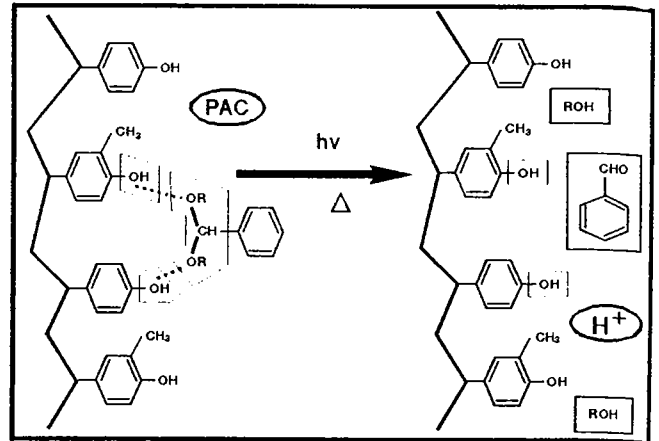


Fig. 2: Basic resist chemistry of RS 1594/E

aldehydes) are very small and significantly more hydrophilic in nature and act as solubility promoting agents.

Poly-(3-methyl-4-hydroxystyrene) (3-Me-PHS)/poly-(4-hydroxystyrene) (PHS) resins

The inadequacy of novolaks as matrix resins in deep UV photoresists results mainly from their poor transparency in the 248 nm wavelength region. Another significant drawback is their rather low thermal flow stability. Polyhydroxystyrenes and their alkylated derivatives found widespread research interest and are accepted as the most promising candidates for deep UV technology. Poly-(4-hydroxystyrene) (PHS) itself is a well investigated phenolic polymer [7-9]. Due to the high solubility of PHS in aqueous-alkaline solutions it is very difficult to find suitable dissolution inhibitors. An additional problem of PHS arises from its high hydrophilicity, which results in both an unbalanced hydrophilic/hydrophobic equilibrium between exposed and unexposed resist areas and between the different ingredients in the resist film. As a consequence an inhomogeneous distribution of resist components or a demixing during processing may result giving rise to the formation of cracks in the remaining parts of the resist material after the respective exposure, bake and development steps. To improve these issues, the phenolic polymer in RS 1594/E contains both, 3-methyl-4-hydroxystyrene (3-Me-HS) and 4-hydroxystyrene (HS) units (Figure 3), which may be applied as a copolymer material or as a blend of the two homopolymers. The obvious advantages of 3-Me-HS/HS copolymers and 3-Me-PHS/PHS blends are an excellent batch to batch reproducibility (copolymerization parameters indicate an

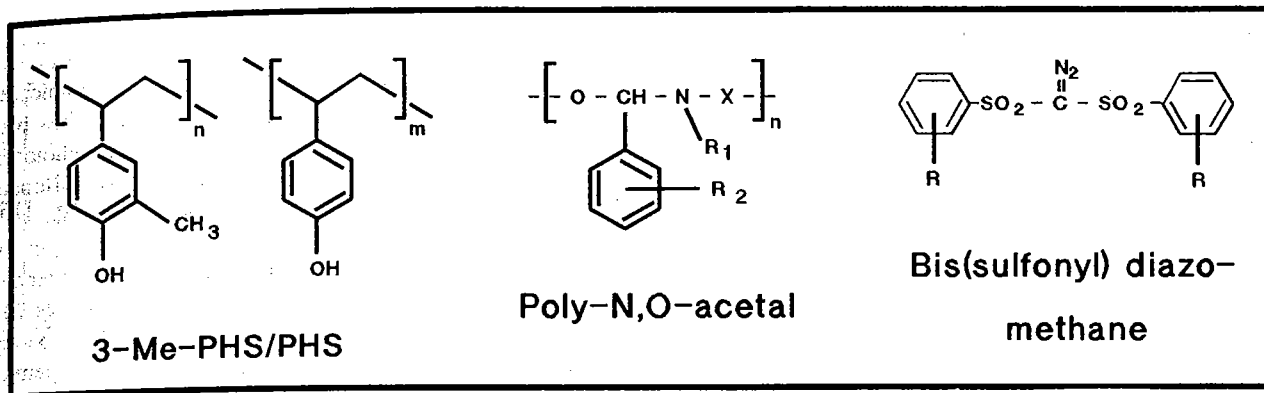


Fig. 3: Resist components in RS 1594/E

ideal azeotropic reaction) and well defined solubility properties (Figure 5). The benefits of 3-Me-PHS have been discussed in previous papers in more detail [10].

The excellent optical properties of 3-Me-PHS give rise to an absorption of approximately $0.18 \mu\text{m}^{-1}$ at 248 nm (Figure 4). The thermal stability is superior to conventional novolak resins. The high glass transition temperature (T_g) of 3-Me-PHS was determined by differential scanning calorimetry to 155 °C, that of PHS to 180 °C. The various copolymers and blends prepared during our studies were found to be within these limits. As an example, the T_g of an 1:1-copolymer was determined to 165 °C. The T_g dependence on molecular weight of the prepared polymers allows a further increase of T_g and therefore of thermal flow stability of the photoresist mixtures. Dry etch stability of 3-Me-PHS based copolymers or blends is comparable to conventional novolaks and DNQ/novolak resists [11]. Additionally, 3-Me-PHS/PHS polymers show excellent film forming and adhesion properties on a large variety of substrates. Finally, PHS is, and 3-Me-PHS probably will become a commercially available product in electronic grade quality.

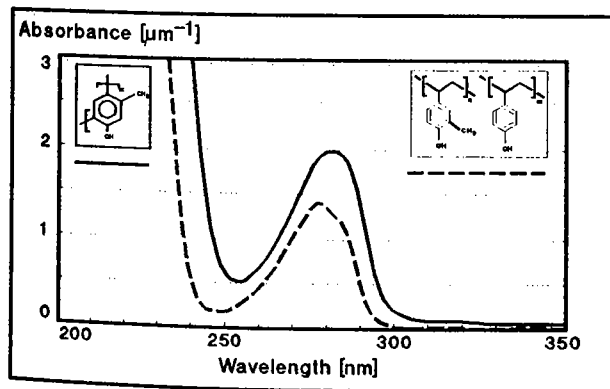


Fig. 4: UV-transparency of a 3-Me-PHS/PHS blend (1/1)

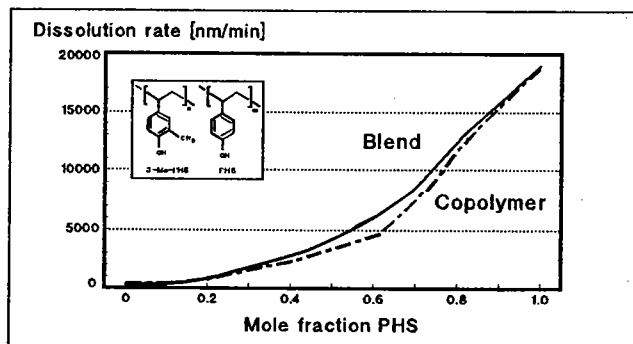


Fig. 5: Dissolution rates of various 3-Me-PHS/PHS copolymers and 3-Me-PHS/PHS blends

Poly-N,O-acetals - tailor-made dissolution inhibitors

In the past many efforts have been made to use the chemistry of acyclic and cyclic, monomeric and polymeric acetals in technical applications [12]. One of the most successful approach was the utilization of acid cleavable acetals in microlithographic systems [13]. During our research activities many attempts were done to find suitable dissolution inhibitors for 3-Me-PHS and its copolymers. Poly-N,O-acetals (Figure 3) show excellent dissolution inhibition properties and form outstanding solubility promoting cleavage products. The adaptability of poly-N,O-acetals to the solubility of different polymers is very impressive and depends mainly on molecular weight (Figure 6). A low molecular weight acetal is capable to reduce the solubility (in 0.27 normality developers) of a 3-Me-PHS homopolymer from around 400 nm/min to 10 nm/min or less by using a 3/1 polymer/acetal ratio. The dissolution rate of 3-Me-PHS/PHS (2/1) or (1/2) copo-

lymers with solubilities of around 2,500 nm/min (2/1) or 6,000 nm/min (1/2), is reduced to 10 nm/min or to a zero dark erosion rate through the addition of an acetal derivative with a higher polymerization degree. All formulations are characterized by excellent homogeneity of the resist film. The adaptability potential makes poly-*N,O*-acetals a convincing dissolution inhibitor for all kinds of phenolic polymers, almost independent from their solubility rate.

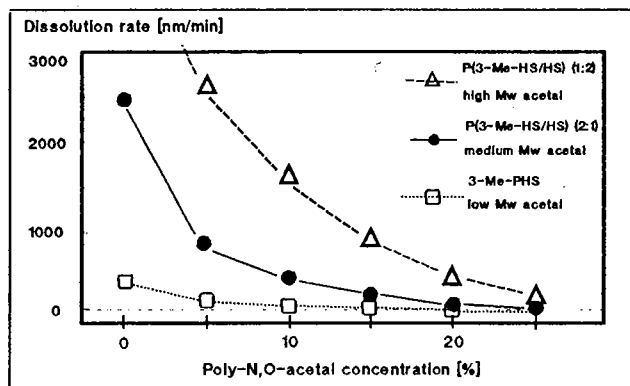


Fig. 6: Dissolution inhibition capability of poly-*N,O*-acetals for various phenolic polymers

The newly developed poly-*N,O*-acetals improve the optical properties of the resulting photoresist formulation as they exhibit neglectable absorptions in the deep UV region. A 1.00 μm thick film, containing a 3/1 polymer/acetal mixture, shows an absorption between 0.15 and 0.25 μm^{-1} at 248 nm, depending on the number and type of substituents at the aromatic ring (Figure 3). Poly-*N,O*-acetals with optimized optical properties result in polymer/acetal films, which exhibit a better 248-nm-transparency than pure 3-Me-HS/HS polymers under the same processing conditions. Acetal polymers are usually viscous liquids, which may cause a significant reduction of the glass transition point of the respective polymer/acetal mixtures. Acetals possessing no aromatic rings in the molecule show a thermal flow stability of below 120 $^{\circ}\text{C}$ in 3-Me-PHS/acetal mixtures (4/1). The incorporation of a substituted aromatic ring into the poly-*N,O*-acetal results, however, in an increase of the thermal flow stability of the corresponding photoresist. The absolute thermal flow stability for a 3-Me-PHS/PHS (1:1) mixture containing 25 % of poly-*N,O*-acetal was estimated to 145 $^{\circ}\text{C}$ (5 μm structures) and is obviously higher than the values for existing DNQ/novolak systems.

Bis(arylsulfonyl)-diazomethanes

During the last few years the number of recommended PAC's for chemically amplified resist systems has been considerably increased. The most utilized photoacid precursors are onium salts [14], nitrobenzyl sulfonates [15], alkyl sulfonates of multifunctional phenols [16], bis(trichloromethyl) triazines [17], brominated phenols [17], disulfones [18], bis(arylsulfonyl)-diazomethanes [19], and *N*-oxysulfonyl- α -pyridones [20]. Aspects like solubility in currently used casting solvents, toxicity, diffusion behavior of the generated acid, and the chemical modification of the molecule chromophore make certain bis(arylsulfonyl)-diazomethanes an interesting class of PAC's for deep UV photoresists. The acid generating mechanism upon irradiation is principally understood and has been discussed in more detail in previous papers [19,20]. A major advantage is the generation of a non-corrosive strong Brønsted acid, which is of particular importance when corrosion sensitive substrates are employed. The generated arylsulfonic acids exhibit a moderate diffusion rate, which has a positive influence on the dark reaction after exposure. Depending on the number and type of substituents attached to the aromatic ring, bis(arylsulfonyl)-diazomethanes exhibit a thermal stability higher than 130 $^{\circ}\text{C}$, in particular higher than 150 $^{\circ}\text{C}$. The literature procedure [21] describes a convenient 3-step synthesis (4-steps, if the preparation of the diazotransfer reagent is included), which offers an easy access to bis(arylsulfonyl)-diazomethanes in good yields. Slight modifications of the published procedure allow a metal-free synthesis and yield materials of high purity. The UV-spectra reveal that the absorption maxima of the UV-transition at longest wavelength are around 255 nm ($\text{C}=\text{N}_2$). Direct irradiation into the carbon diazo bond is mainly responsible for the bleaching behavior of bis(arylsulfonyl)-diazomethanes (BAS-DM) at the exposure wavelength and for the unexpected high photoacid generating efficiency. A more detailed investigation of the photoacid generating capability in accordance to the method developed by Buhr and Dammel [17] evidenced their superior properties in comparison to other selected classes of PAC's (Figure 7). Only triazines (formation of hydrochloric acid) and the pyrogallol tris(methane sulfonate) (formation of methane sulfonic acid) show a higher photoacid generating efficiency, while tribromomethane phenyl sulfone (TBMPS), arylsulfonyl-arylcarbonyl-diazomethanes (ASAC-DM), or 2,1-diazonaphthoquinone-4-sulfonic acid esters have a minor acid generating capability than BAS-DM's. In addition, the preferred diazo methane compounds have also an extraordinary chemical stability in the casting solvent.

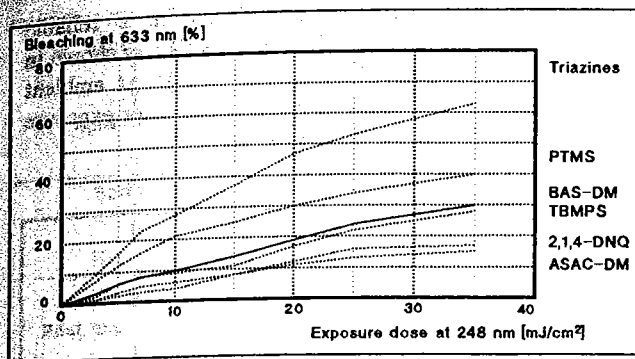


Fig. 7: Photoacid generating efficiency of bis(arylsulfonyl)-diazomethanes in comparison to other classes of PAC's

3. Critical Process Parameters

3.1. Experimental Details

Photoresist solutions were prepared by dissolving the components in propylene glycol monomethylether acetate (PGMEA) and filtered through 0.2 μm PTFE filters before use.

Silicon substrates were subjected to a vapor phase HMDS treatment. Excess of HMDS was removed from the substrate by an additional thermal treatment. The resist was coated to yield a film thickness of 1.00 μm after application of a softbake at 120 $^{\circ}\text{C}$ for 60 s on a hotplate. A Süss mask aligner MA 6 (vacuum contact printing method), equipped with a KrF excimer laser LPX 110 iCC (Lambda Physics), or a KrF excimer laser stepper from ASM Lithography (PAS 5000/70, 0.42 NA) served as irradiation tools. After the application of a PEB at 60 $^{\circ}\text{C}$ for 60 s, or 80 $^{\circ}\text{C}$ for 60 s, respectively, the material was developed for 60 s at 21 $^{\circ}\text{C}$ with a commercial grade MIF developer (AZ^R 312-27 MIF) containing 2.38 % TMAH in the immersion mode and rinsed with distilled water. Film thickness measurements were performed using a Rudolph FTM. SEM pictures were taken in the AZ application laboratories in Wiesbaden, Germany, using a scanning electron micrograph (SEM) Hitachi S 800. Depth of penetration (DOP) tests were performed using a dark field mask with fields of increasing opacity. UV-spectra were recorded using a Perkin-Elmer Lambda 2 UV/VIS Spectrophotometer and quartz wafers. Film thickness was measured mechanically by using a Sloan Dektak II apparatus. Delay time intervals (see Figure 10 and chapter 3.4.) were within the following limits: $I_1 < 30$ min, $I_2 < 2$ h, $I_3 < 3$ min, and $I_4 < 5$ min.

Deviations from experimental details are discussed in the text. Table 1 gives the recommended process conditions for RS 1594/E.

3.2. Dissolution Rate Ratio

A prerequisite to achieve optimum resolutions in photoresist materials is a strong dissolution rate ratio between exposed and unexposed resist areas. In conventional DNQ/novolak materials the excellent dissolution rate ratio is caused by the photochemical induced transformation of the DNQ dissolution inhibitor into the more soluble indenecarboxylic acid [22] and the chemical reactions and/or developer/resist interactions during aqueous alkaline development [23].

Coating:	3400 rpm
Prebake:	120 $^{\circ}\text{C}$ /60 s
Film Thickness:	1.00 micron
Exposure:	KrF (248 nm) Excimer Laser
Exposure Dose:	20 - 30 mJ/cm ²
PEB:	60 $^{\circ}\text{C}$ - 80 $^{\circ}\text{C}$ /60 s
Development:	60 s, Immersion, AZ ^R 312-27 MIF
Contrast:	> 4.5
Dark Erosion:	0 - 10 nm/min

Tab. 1: Recommended process conditions for RS 1594/E

A major target was the improvement of the dissolution rate ratio in preliminary versions of RS 1594/E. Depending on the HS and 3-Me-HS copolymer composition, the dissolution rate of the poly(hydroxystyrene) matrix resins in 2.38 % TMAH developers is adjustable between 400 nm/min and several thousand nm/min (Figure 5). The poly-*N,O*-acetal is capable to reduce the dissolution rate of the polymer/acetal mixtures down to zero values (Figure 6). The photogenerated acid effects an efficient bond cleavage of the acetal to solubility promoting agents. The dissolution rate in the exposed areas is between 10,000 and 50,000 nm/min, depending on the PEB conditions, the polymer properties, and the polymer/poly-*N,O*-acetal ratio. High molecular weight poly(hydroxystyrene)s may decrease the dissolution rate ratio by reducing both the solubility in the unexposed and much stronger in the exposed areas. HS containing copolymers are more soluble than 3-Me-HS homopolymers. Standard dissolution rates of the exposed RS 1594/E are around 30,000 nm/min. Depending on the dark erosion rate (for example: 5 nm/min) acetal-based deep UV resists have

dissolution rate ratios of $> 5,000$ and achieve values typical for high performing DNQ/novolak systems.

3. 3. Influence of Post Exposure Bake on Photosensitivity and Dark Reaction in Acetal-Based Photoresists

A characteristic property of chemically amplified photoresist materials is the dependence of photospeed on the PEB temperature. Figure 8 shows the different photosensitivity values for patterning equal $0.40 \mu\text{m}$ line & space structures at various PEB temperatures.

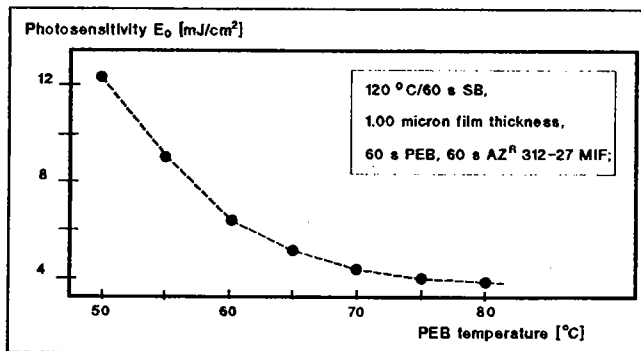


Fig. 8: Photosensitivity dependence on PEB temperature

The sensitivity curve can be divided into three different sections. The first section includes the PEB temperature interval between $50 \text{ }^\circ\text{C}$ and $60 \text{ }^\circ\text{C}$, where a strong dependence of photosensitivity on PEB temperature is observed. An increase of $10 \text{ }^\circ\text{C}$ (all 1 min on a hotplate) results in an increase of photosensitivity by a factor of 2. The change of the PEB temperature between $60 \text{ }^\circ\text{C}$ and $70 \text{ }^\circ\text{C}$ has only a moderate influence (50 % increase in photospeed by a $10 \text{ }^\circ\text{C}$ higher PEB). The photosensitivity change in the third section ($70 \text{ }^\circ\text{C}$ to $80 \text{ }^\circ\text{C}$) is reduced to a variation within 10 % and nearly neglectable. Using PEB temperatures $> 80 \text{ }^\circ\text{C}$, some concurrent cross-linking reactions are observed, which may deteriorate the image quality. In general, prolonged bake times result in much smaller sensitivity changes.

The observed photospeed changes upon PEB temperature variations are mainly attributed to the acetal cleavage kinetics. The relatively low activation energy for the cleavage of the acetal moiety is responsible for the system inherent dark reaction of acetal-based photoresists. The cleavage reaction of the acetal into aldehyde and alcohol takes place immediately after exposure. UV-monitoring of this reaction shows a continuous increase of the absorbance at 248 nm due to aldehyde formation. Extinction coefficients of aldehydes are typically higher by a factor of 10 than of the corresponding acetal

precursor. The increase of absorbance is a reliable indicator for the proceeding cleavage reaction as shown in Figure 9 ($I_3 = 0 \text{ min} \hat{=} \text{exposure time}$). At ambient temperature the reaction starts immediately after exposure and is completed after about 120 min.

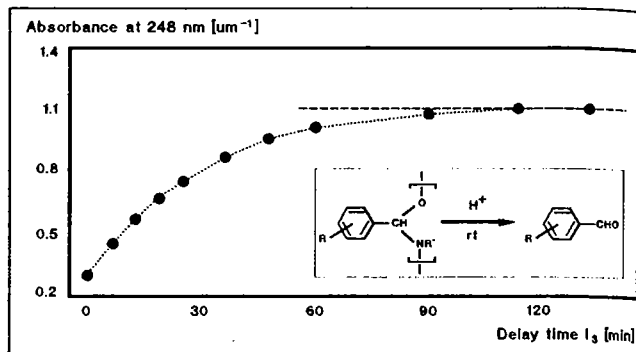


Fig. 9: Dark reaction in acetal-based photoresists

The absorbance increase in the 248 nm region from $0.25 \mu\text{m}^{-1}$ to $1.1 \mu\text{m}^{-1}$ depends on the optical properties of the resist components, especially on the acetal substitution patterns, and on the polymer/poly-*N,O*-acetal ratio. The time required to complete the reaction (120 min) is controlled by cleavage kinetics and the mobility of the generated acid. The acid mobility is controlled by the selected softbake conditions, acid size and acid strength. The lithographic performance of RS 1594/E formulations containing certain useful organic additives is not influenced by the dark reaction. The PEB corresponds to a dark reaction with significantly shortened time frames, therefore no difference is observed in the exposed areas between the application of a slow dark reaction at ambient temperatures or a short post exposure bake. Using an optimized PEB temperature no solubility change is observed in the unexposed image areas. This implies that the acid diffusion into the unexposed regions is very slow at room temperature, or that the diffusion is markedly hindered by the interaction of the produced acid with the additive.

The dark reaction phenomena is characteristic for cleavage reactions in acetal based resists, which require a low activation energy, but it does not affect the lithographic performance. The reaction mechanism suggests that a PEB step is not definitively mandatory.

3. 4. Critical Process Intervals

Figure 10 shows a complete process flow chart including the intervals before (shelf life) and during processing, which might have an influence on the lithographic performance.

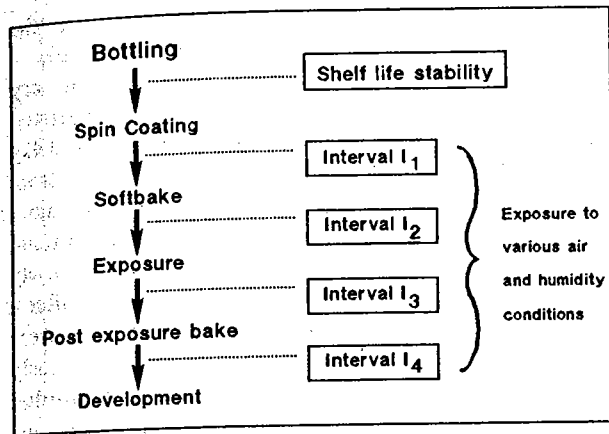


Fig. 10: Process flow chart of RS 1594/E including delay times.

Shelf life stability

The nature of chemical amplified materials may give rise to the expectation that both the solution and film shelf life stabilities are much lower than that of conventional DNQ/novolak materials. Even small traces of acidic impurities might induce a cascade of cleavage reactions, which result in a tremendous change of photosensitivity, dissolution rate ratio, optical properties and other effects degrading the resist performance.

As the most critical factors traces of acid, coming from the synthesis of the phenolic polymer and small amounts of residual water were identified. Adequate purification and drying of the raw components result in formulations with no change in photosensitivity and absorption upon at least four months of resist storage. Figure 11 shows the relationship between dissolution rate ratio and shelf life of RS 1594/E. The first tests were made under standard laboratory conditions and indicated that the dissolution rate of the photoresist depends strongly upon the ubiquitously available water from the environment (polymer solutions checked at the same day show a nearly identical dissolution behavior). This effect is well known from several types of novolaks [24]. Similar to DNQ/novolak systems acetal-based photoresists require an external source of water for the solubility change after irradiation. The strong humidity control of a clean room atmosphere gives much more uniform results and shows no difference in dissolution rate (Figure 11) and in photosensitivity within eight weeks. Traces of aldehyde, which may result from an unoptimized poly-*N,O*-acetal synthesis were identified as an additional critical factor. Oxidation of the aldehyde present in these materials can be transformed to the corresponding benzoic acid, which

is acidic enough to bring about a very slow, but detectable acetal cleavage upon standing at room temperature. Meanwhile, an improved purification method of the poly-*N,O*-acetal, which avoids traces of aldehyde in the resist formulation, has been developed.

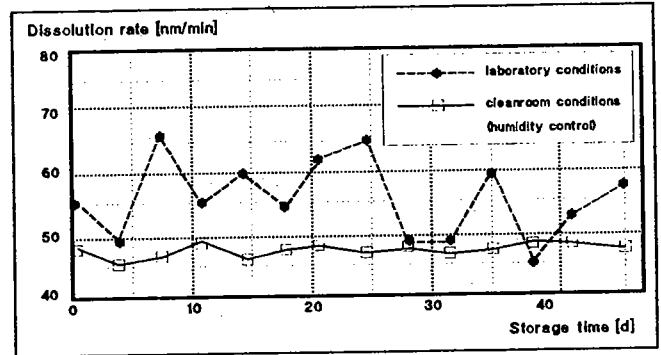


Fig. 11: Dissolution rate of an acetal-based photoresist with extended storage times under different humidity conditions.

Interval I₃ between exposure and post exposure bake

Interval I₁ between coating and softbake as well as the interval I₂ between softbake and exposure were found to be less critical to the formation of a surface inhibition layer and the resulting formation of "T-shaped" profiles within common handling times. The most important interval with respect to resist profile deterioration is the delay time I₃ between exposure and the subsequent baking step.

The so-called delay time effect stands for at least two, but often three different effects, namely

(a) the increasing formation of a region on the resist surface, having a thickness of around 20 to 50 nm and showing a strong reduced solubility in comparison to lower parts of the exposed area,

(b) a linewidth decrease, and

(c) a significant change in resist sensitivity,

which are initiated or amplified upon application of extended interval times after exposure.

Surface inhibition layer

This phenomenon is caused mainly by environmental effects [25]. Our investigations confirmed previous work and revealed that the exposure of coated wafers to a

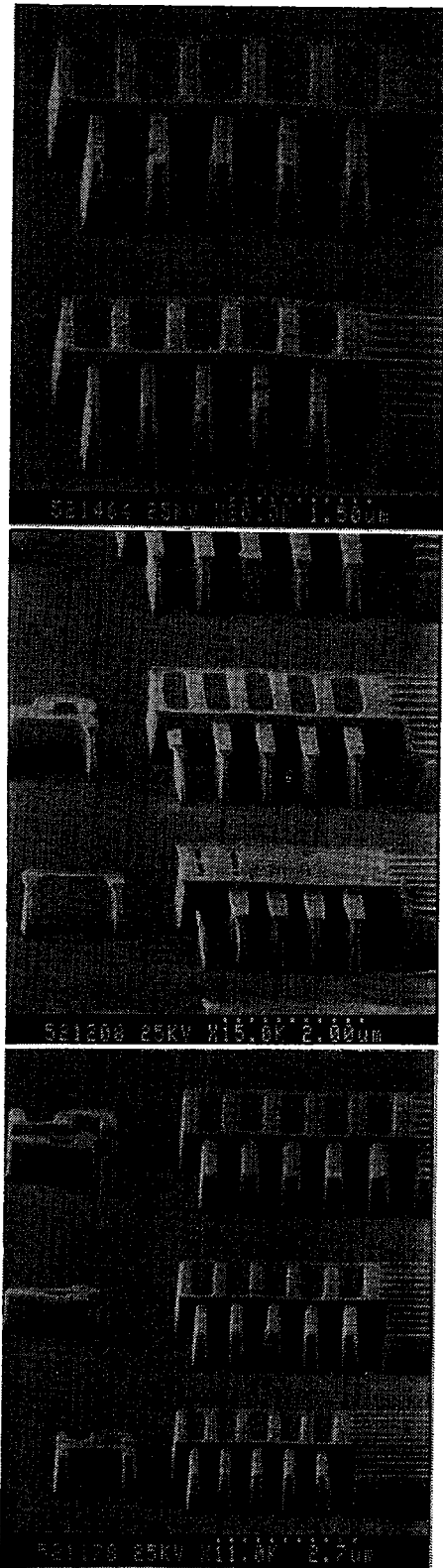


Fig. 12: Influence of additives in RS 1594/E on the formation of "T-shaped" profiles upon extended interval I_3 . Top: $I_3 = 0$ min, additive; middle: $I_3 = 60$ min, no additive; bottom: $I_3 = 60$ min, additive.

base containing atmosphere, e.g. processing in presence of amine containing developers, causes significant deterioration of the resist profile within very short exposure times. The strength of the photogenerated acid has a significant influence on the degree of delay time stability. Stronger acids like those produced from onium salt photoacid generators exhibit a more pronounced deterioration of resist profiles than sulfonic acid precursors during the same interval. In each formulation of RS 1594/E containing no additive, after a minimum of 20 - 30 min "T-shaped" profiles were observed. Although this is much better than previous published results [26], efforts were made to further enhance the resist insensitivity towards delay intervals. Our presently optimized resist formulation uses a specific organic additive and allows processing with an interval of at least 60 min without the generation of a surface inhibition layer (Figure 12).

Another efficient method to reduce the influence of airborne contaminations is the use of a top antireflective coating (TARC). The water soluble TARC solution will be coated immediately after softbaking the resist as a thin overcoat onto the resist film. Processing under standard conditions gives a stable image for more than 120 min. After 240 min only a slight linewidth broadening on the top of the line was observed and indicates the beginning of resist profile deterioration. The use of TARC overcoats has also some positive effects, if patterned over high reflective substrates and/or over topography is desired.

Linewidth decrease

Slimming of resist lines with extended interval I_3 was a serious problem during performance optimization. An intensive investigation revealed that linewidth decrease depends on more than one factor, namely acid mobility. As expected, the substitution of small acids, such as methane sulfonic acid, by bulky acids, e.g. 4-tert-butyl benzoic acid showed a reduced slimming of the resist lines. A much stronger performance increase was achieved, however, through coformulation of an additive (Figure 13). The use of a bulky acid and an additive was much more near the ideal behavior than other approaches. After 90 min a linewidth decrease of only 18 % from the former $0.40 \mu\text{m}$ line was lost. This equals to a resulting linewidth of $0.33 \mu\text{m}$ in the resist. The 10 % variation from the nominal linewidth ($0.36 \mu\text{m}$ line/ $0.44 \mu\text{m}$ space) was obtained after 22 min. The successful application of additive coformulation is shown in Figure 12.

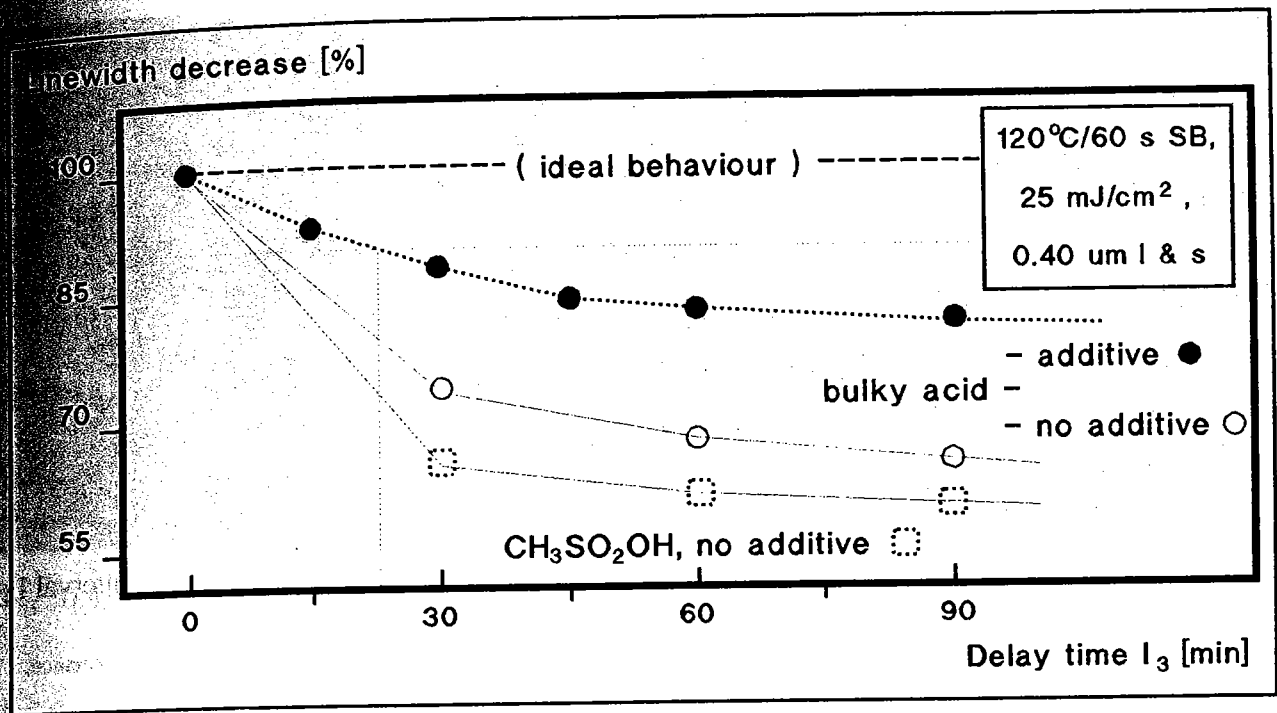


Fig. 13: Linewidth decrease vs delay time I_3 in dependence on different resist modifications.

Change in photosensitivity

The sensitivity change upon prolonged interval I_3 documents a major problem for cassette to cassette operation, but has no influence on wafer to wafer operation, if the wafer are subjected to a PEB immediately after irradiation.

The predevelopment interval I_4

The predevelopment interval I_4 shows some interesting aspects of acetal chemistry. UV-monitoring of the exposed and baked (PEB) photoresist films shows an unexpected result, which is outlined in Figure 14.

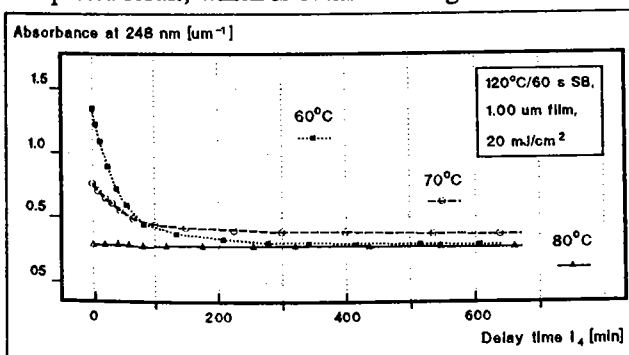
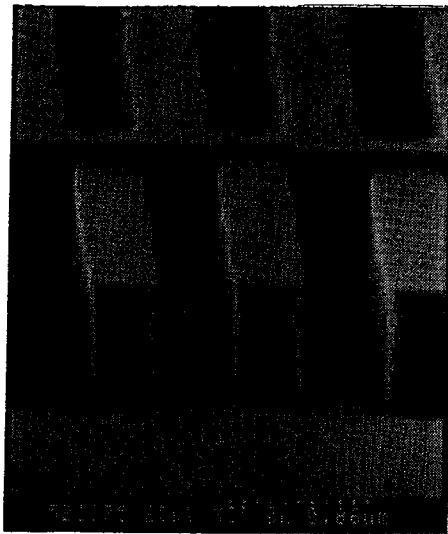


Fig. 14: Absorbance at 248 nm vs predevelopment interval I_4 in dependence on PEB temperature.

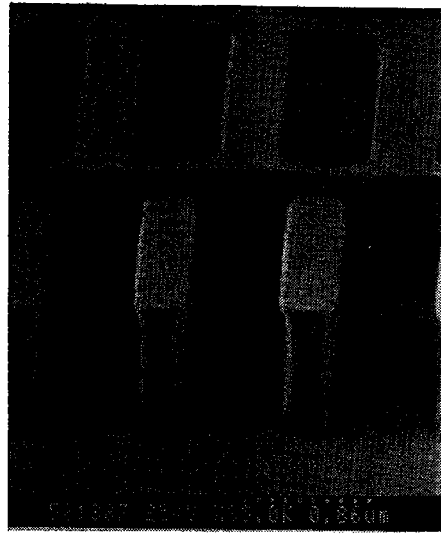
The curve behavior after a 60 °C/60 s PEB leads to the conclusion, that the system has not yet reached a stable equilibrium. At a 80 °C/60 s PEB step the reaction seems to be completed, because no change in UV-absorbance could be detected. The lithographic approach to fix this effect is shown in Figure 15. Also a noticeable linewidth decrease accompanied by the formation of a surface inhibition layer was observed. The additive coformulation as well as a PEB of 80 °C/60 s of a additive free formulation guarantees a stable system.

4. Lithographic Performance

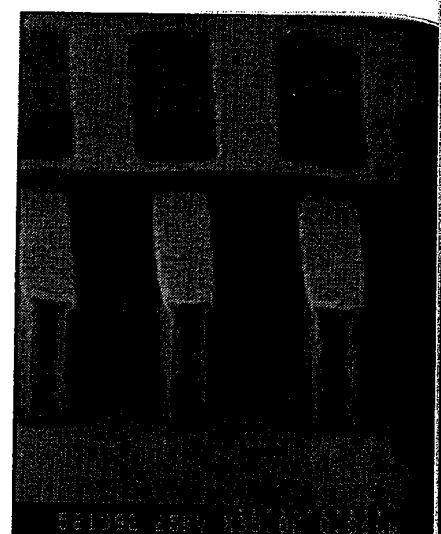
The most important requirement a deep-UV photoresist has to fulfill is the resolution of 0.35 μm line and space pattern. Concerning terms of reproducibility and process reliability a minimum resolution of 0.30 μm lines and spaces or even below is required. KrF-(248 nm)-Excimer laser exposure (ASM-L, 0.42 NA) of a RS 1594/E resist film with an exposure dose of 25 mJ/cm² and processed as described above (chapter 3.1.) give a resolution of at least 0.30 μm lines and spaces, as shown in the overview in Figure 16. Using a modified formulation (higher concentration on photoacid generator) an exposure dose of only 10 mJ/cm² is necessary to obtain resist structures with really vertical sidewalls. Figure 17 demonstrates the



0 min delay interval I_4



60 min delay interval I_4



120 min delay interval I_4

Fig. 15: Influence of the predevelopment interval I_4 after a 60 °C/60 s post exposure bake on resist performance.

good profiles of the resulting lines even under overexposed conditions.

Other possibilities to increase the resolution limit base mainly on an optimization of the aerial image. An easy way to achieve this objective is a decrease of the resist thickness of the coated photoresist. This method is limited by practical aspects concerning the subsequent process steps after development. The reduced resistance of thinner films against exothermic processes like dry etching is one example. More promising technologies,

which saw a renaissance during the last years, were not based on an improvement of resist performance, but on an optimization of exposure equipment and optical parameters. A promising technology to achieve a better resolution by improvements of the optical image transformation is the use of the phase shift mask technology. The different PSM technologies are only for special pattern transfer. One of the most versatile PSM technologies is the Levenson-type PSM [27]. If the resolution potential of the selected resist material is qualified enough, the application of Levenson-PSM can

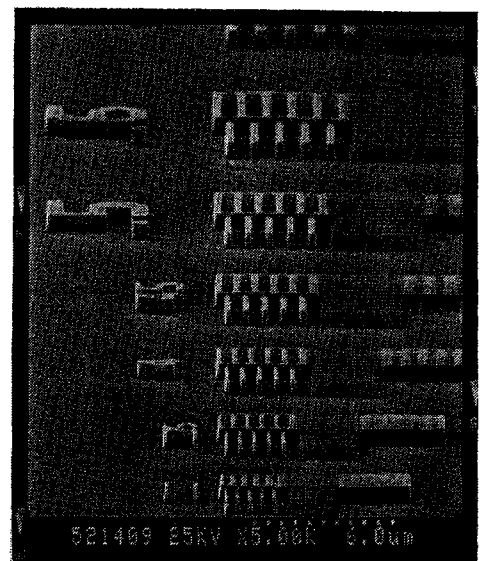
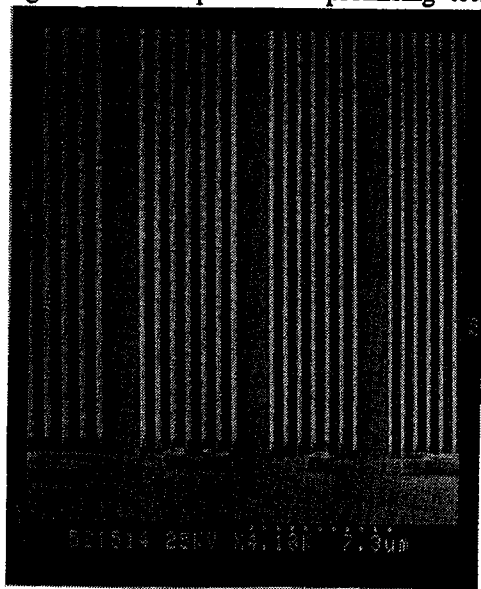
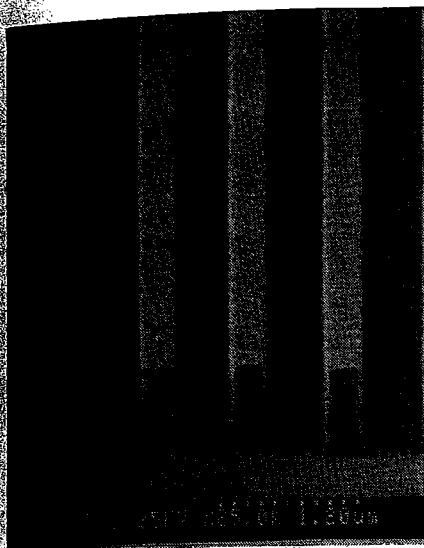
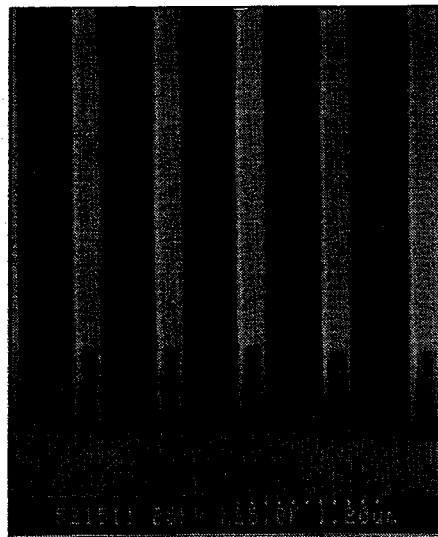


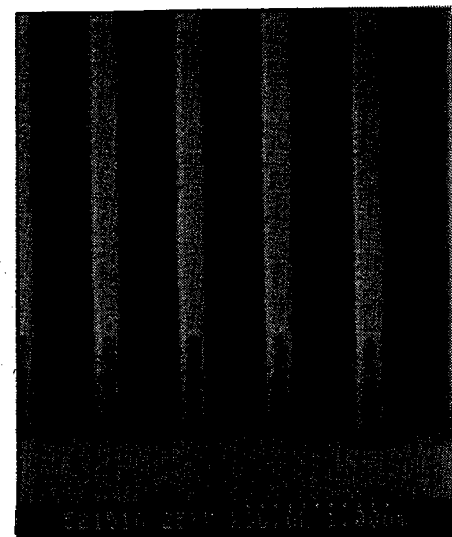
Fig. 16: SEM pictures of different line/space pattern of RS 1594/E.



0.45 μm l & s



0.40 μm l & s



0.35 μm l & s

Fig. 17: Resolution of RS 1594/E.

give an additional improvement in resolution and will shift the resolution limit into the quatermicron region. First attempts of RS 1594/E with PSM are depicted below.

5. Conclusion

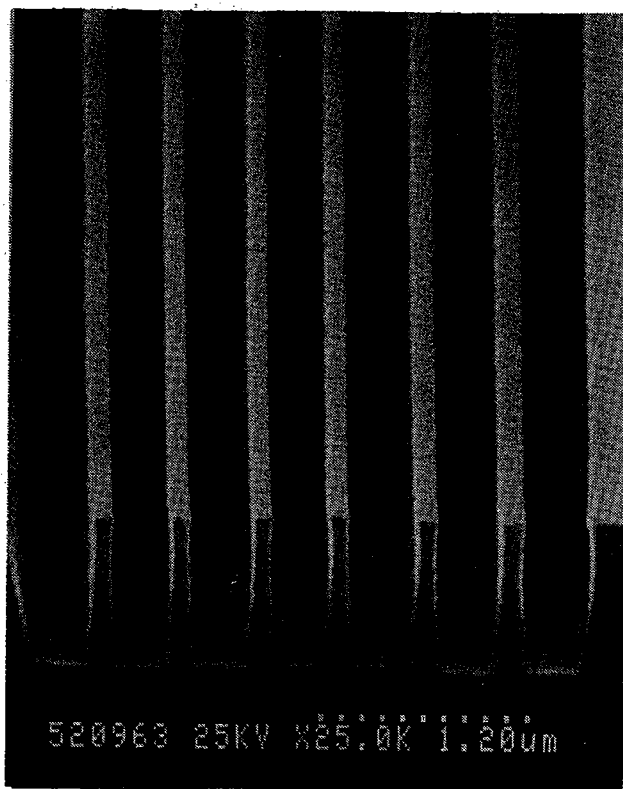
A novel positive tone photoresist based on the principle of chemical amplification has been developed. RS 1594/E consists of a phenolic polymer, a dissolution inhibitor, and a photoactive compound. The dissolution inhibition of the polymer is achieved using a newly designed poly-*N,O*-acetal, which undergoes an efficient bond cleavage in the presence of a photogenerated acid and leads to the formation of solubility promoting fragments. The influence of various resist components were discussed with respect to selected lithographic performance parameters. Dissolution rate ratio between exposed and unexposed resist areas, post exposure bake temperature, as well as different delay times were determined as the most critical process parameters for the processing of RS 1594/E. The process interval of greatest interest, the time between exposure and PEB, has been discussed in more detail. Prolonged intervals are found to be mainly responsible for an increased formation of an insoluble surface inhibition layer ("T-topping"), a strong change in photosensitivity and a significant linewidth decrease. Additive coformulations of RS 1594/E show a noticeable divergence in delay

time behavior than additive free resist formulations. Latent image stability is improved even after 60 minutes delay between exposure and PEB. The linewidth decrease is markedly reduced and neither the surface inhibition effect, nor a formation of "T-shaped" profiles have been observed after this interval. SEM pictures of 0.24 μm , 0.26 μm , and 0.28 μm line and space patterns demonstrate the high resolution capability of RS 1594/E.

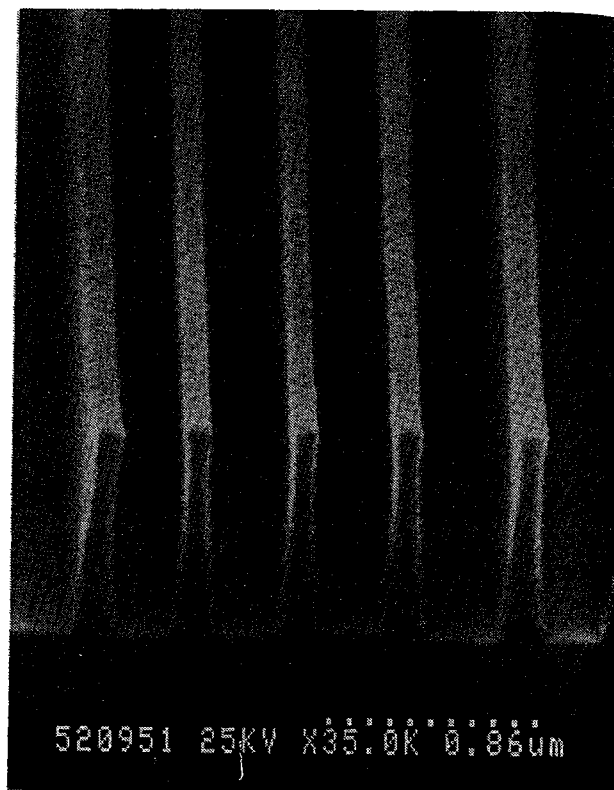
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0.26 μm l & s



0.24 μm l & s

Fig. 18: Resolution potential of RS 1594/E.

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