AN OVERVIEW OF RESIST PROCESSING FOR DEEP-UV LITHOGRAPHY

OMKARAM NALAMASU, MAY CHENG, ALLEN G. TIMKO, VICTOR POL, ELSA REICHHANIS, and LARRY F. THOMPSON

AT&T Bell Laboratories, Murray Hill, New Jersey 07974

Continued advances in microelectronic fabrication are trying the limits of conventional lithographic technologies [1]. The traditional diazonaphthoquinone/novolac resist materials are not suitable for use with the deep-UV exposure tools both from the absorption and sensitivity considerations [2]. New resist materials and processes are necessary to fully utilize the potential of deep-UV microlithography, a more promising technology for the production of sub-0.5μm geometries. The advent of resist materials based on chemical amplification principle [3,4], where one photochemical event leads to a cascade of subsequent events causing a solubility differential, exhibit high resolution, excellent sensitivity and good etch selectivity required for deep-UV lithography.

While process sequence for chemically amplified materials is similar to conventional positive resist process sequence, post-exposure bake (PEB) assumes the role of effecting a solubility differential by means of thermally activating the acid catalyzed crosslinking or deblocking reaction. The PEB parameters, the delay time between exposure and post exposure bake (post exposure delay time, PED) and the inherent chemistry of the resist system greatly effect the process performance.

This paper summarizes the process characteristics of select positive and negative deep-UV resists, and attempts to correlate the results to the chemical design of the individual resists.
INTRODUCTION

New resists and process are required for deep-UV lithography to reach its full potential since conventional novolac based materials are too opaque for use at wavelengths below 300 nm [1,2]. Two major approaches can be adopted to overcome the limitations of resist materials for deep-UV applications. While the use of surface imaging techniques [3,4], relaxes the depth-of-focus constraints and topography considerations, reproducible residue-free sub-0.5µm resolution at acceptable doses (< 50 mJ/cm²) has not been demonstrated.

Single layer chemically amplified systems are one means of accommodating the high sensitivity, low absorbance requirements of deep-UV lithography [1]. Chemical amplification is a term coined to describe the catalytic nature of events taking place in a resist system [5,6]. In these schemes, a photogenerated species, mostly an acid molecule, catalyzes several crosslinking [7] or deblocking [8-13] reactions during PEB step to introduce differential solubility. Since the solubility differential is effected at the PEB step, PEB parameters such as temperature, time and type of bake are critical process issues. An additional critical dependence on the post-exposure delay time (delay time between exposure and PEB) [10,11], was also discovered in the case of chemically amplified positive resists designed on acid catalyzed deprotection chemistry.

This paper will summarize our work in the process development of chemically amplified positive resist materials and draws a parallel to either other published work or our own experiences on other deep-UV positive and negative resist materials, where appropriate [9,12,13-15]. The most closely examined positive resist materials here are formulated with poly (t-butoxycarbonyloxystyrene-sulfone) (PTBSS) copolymer with either the ionic triphenylsulfoniumhexafluoroarsenate onium salt (Ph₃S⁺AsF₆) or the organic covalently bound nitrobenzyl ester photoacid generators (Scheme I). SNR 248 is a negative deep-UV resist consisting of a poly(vinyl phenol) resin, HBr generating PAG and melamine crosslinker (Scheme II) and is available from Shipley Co. [7]
EXPERIMENTAL

Materials

PTBSS copolymers were prepared from t-Boc styrene and sulfur dioxide using a literature procedure [16]. The onium salts were prepared by the general method described by Crivello [17]. Nitrobenzylester PAG materials were synthesized as described previously [18].

SNR 248 is a commercially available negative resist from the Shipley Co. and was used as such with an optimized process.
LITHOGRAPHY

The resist solutions were prepared by dissolving the matrix copolymer (15-20 wt%) in a solvent followed by the addition of 5 wt% arsenate onium salt or 6 mole % of nitrobenzyl sulfonate ester PAG. The solutions were filtered and spin-coated on appropriate substrates.

The substrates were typically primed with HMDS (hexamethyldisilazane) in a Y.E.S. (Yield Engineering System, Inc.) oven prior to the application of the resist. The PTBSS coated wafers were exposed on a GCA laserstep prototype deep-UV exposure tool operating at 248 nm, post-exposed baked at 115°C/30 sec and developed in 0.17 N TMAH (tetramethylammonium hydroxide) for 30 sec to generate positive images. In the case of SNR 248 material, resist-coated substrates were pre-baked at 90°C/1 min., exposed with deep-UV light, post-baked at 120°C/90 sec. and spray developed for 120 sec. with 0.15N TMAH.

The delay time between exposure and PEB was varied from 1 to 15 minutes and its effects were characterized by linewidth data and image quality. In some experiments, wafers were coated with Brewer Science ARC (Anti-Reflective Coating) materials and baked prior to the application of PTBSS resist and overcoat and processed as mentioned above.

RESULTS & DISCUSSION

Resist Chemistry

The generic design on which most of the positive acting chemically amplified materials are based constitutes of blocking a hydroxy, carboxyl or an imido group of an aqueous base soluble polymer or copolymer network with a protective group that imparts aqueous base insolubility [1]. The protecting group, is additionally acid labile. Photogeneration of acid from a PAG followed by a PEB effects catalytic removal of the protecting group with high turnover rates and generates a base soluble exposed region. A variety of PAG molecules can be used for positive acting systems, including ionic onium salts, and covalent nitrobenzyl esters, sulfonates, disulfones and imino sulfonates [1].

Negative acting chemically amplified resists can also be two or three component systems comprising of a PAG, a base soluble matrix polymer with latent electrophiles [19] or a base soluble matrix polymer with an added crosslinker such as melamine. The only commercially available
deep-UV resist, SNR 248, consists of a poly (vinyl phenol) binder with a HBr acid generator and melamine crosslinker (scheme II) [7]. Dissolution inhibition in the exposed and baked regions is achieved by two pathways; an increase in polymer molecular weight with the concomitant depletion of phenolic hydroxide moieties [20].

Process Performance

The positive deep-UV resist examined here utilized PTBSS as the matrix resin (Scheme I). Formulation with triphenylsulfonium hexafluoroarsenate (Ph3S+ AsF6−) onium salt PAG afforded a very sensitive, high resolution and high contrast resist system. The resist could resolve 0.35µm line/space features with vertical wall profiles in 1µm films at an exposure dose of 10 mJ/cm² and exhibited excellent tolerance with respect to process variables such as softbake temperature and time, PEB temperature and time and developer concentration and time. Exposure and focus latitudes were also good [10].

However, this onium salt based resist system did have three major limitations, 1) the presence of arsenic is perceived to be a potential device contaminant, 2) the process performance severely degraded as the elapsed time between exposure and PEB (hereafter referred to as post-exposure delay time, PED) is increased and 3) lost thickness corresponding to the t-Boc groups rapidly during the initial stages of pattern transfer [10].

Subsequent process development work using covalent, metal ion free nitrobenzyl ester PAG material with PTBSS addressed the issue of metal-ion contamination and also provided a sensitive and high resolution resist system capable of resolving 0.3µm line/spaces and 0.4µm contacts in 1µm films at exposure doses of 20-50 mJ/cm² [11]. It was, however, subject to similar PED time and pattern transfer effects as its arsenate, onium salt counterpart. The use of overcoat materials dramatically alleviated the PED issue for both the onium salt and nitrobenzyl ester formulations [11]. PTBSS resist formulations also exhibited wide latitude with respect to developer concentration, time and temperature. PEB latitude was also good. Additionally, excellent latitude was also available for contact hole definition with these materials (Fig. 1). The issues presented here regarding PTBSS/PAG deep-UV resists are generic to positive, chemically amplified resist systems based on acid catalyzed deprotection, and novel chemical and process solutions are being developed [21].
Several reports have also been published on the use of SNR 248 for deep-UV lithography [7,14,20]. Excellent resolution, sensitivity, process control and dry etch resistance were demonstrated. Additionally, SNR 248 did not exhibit any dependence on PED time for up to 1 hour. The inherent design of acid activated crosslinking chemistry, however, limits the resolution and latitude of the contact hole printing (Fig. 2). Accordingly, very little or no process latitude was observed with respect to exposure and focus parameters for the definitions of 0.5μm or smaller contact holes [22]. Some additional issues that need to be considered with negative resists are that 1) they are hard to strip, especially after pattern transfer and 2) the use of AR (anti-reflection) coatings result in retrograde image profiles requiring overexposure of pattern to reduce the toppling of the outermost features in a line/space stack [14].

Fig. 1 Exposure latitude for contact hole definition with metal-ion free PTBSS resist formulation.

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Perhaps the best way to address the issues related to deep-UV resist processing is by the examination of individual process events in the process sequence and subsequent correlation of them to the resist chemistry. Hence, the processing issues that are most relevant to deep-UV chemically amplified resist materials will be discussed under the headings of adhesion, PED (or surface inhibition) effects, PEB, development, thin film interference and pattern transfer effects.

Adhesion

The adhesion properties of the hydrophobic matrix resins typically used in chemically amplified positive resist formulations are significantly different from those of hydrophilic (and slightly acidic) novolac type resins. Incorporation of even moderately hydrophilic moieties e.g. sulfur dioxide into the backbone of poly(t-butoxycarbonyloxystyrene), seemed to provide some improvements in the adhesion of the resist to various device substrates. Priming with HMDS under relatively aggressive conditions was required to achieve acceptable adhesion for PTBSS resists.

Adhesion requirements of negative resists based on polymers such as poly (vinyl phenol) are equivalent to those of conventional novolac based resists.

Fig. 2  Definition of 0.5 µm contact holes at optimum focus with SNR 248 at doses 15 and 16 showing poor latitude.
Post-exposure Delay Time (PED) or Surface Inhibition Effects

The time delay effect manifests itself as T-shaped resist profiles and aqueous base insoluble surface residues, which are aggravated as the delay time is increased. PTBSS resist formulations were quite sensitive to such time delay effects. Delays greater than 1 and 3 mins. for onium salt and nitrobenzyl ester formulations, respectively, were detrimental to the resist performance and resulted in total "bridging" or "filling" of the trenches of sub-micron line/space pairs (Fig. 3) [10,11]. Interestingly, the film thickness loss in the exposed regions during PEB was PED independent within experimental accuracy yet the delay affects both the ability of the developer to solubilize the exposed and baked regions as well as the quality of images in the resist.

Data from a variety of analytical techniques concomitant with exposure of the resist under various environmental conditions in an environmental chamber excluded the role of humidity and oxygen and confirmed that the presence of basic vapor in the ambient severely degraded the resist performance and time delay latitude.

For instance, a HMDS concentration of only 15 ppb reduced the PTBSS resist sensitivity by at least a factor of 2, severely degraded image quality (Fig. 4) and generated substantial amounts of surface residue. A decrease in HMDS concentration to <5 ppb led to enhanced sensitivity, and images with straight wall profiles were obtained. Other examples of airborne contaminants include
N-methyl pyrrolidone (NMP, a solvent typically used in resist strippers), and N,N-dimethylformamide (DMF, a commonly found solvent in weld-on chemicals). Even materials such as fresh latex paints contain sufficient quantities of amine to have a pronounced effect on resist performance [11,21].

Considering the total concentration of acid generated in a 1µm film on a 5" substrate is only $10^{-5} - 10^{-6}$ mmol., and that ppb levels of basic vapor contaminants in air can form several monolayers of material on the resist surface within seconds, it is conceivable that some of the photogenerated acid is neutralized during the time delay. Since the deprotection turnover rates are very high ($1000)^{23}$, even a small decrease in acid concentration can cause significant decrease in the t-Boc deprotection at the resist surface resulting in base insoluble residue. Small variations in t-Boc concentration in the matrix polymer can profoundly effect the solubility characteristics as the dissolution mechanism exhibits a step function like behavior requiring greater than 95% t-Boc deprotection to achieve aqueous base solubility [10].

While the PED issues appear to be generic [1] to the acid catalyzed chemically amplified systems they are truly apparent in only positive acting systems. The presence of ppb levels of bases in environment not only deteriorated the resist performance during the PED, but also during the time interval between coating and pre-baking [21]. This indicates that significant amounts of bases are adsorbed on the resist surface after coating and softbake and that they deactivate the acid generated during exposure.

We have investigated PED effect for upto an hour on SNR 248 by monitoring the stability of the linewidth (0.5µm feature) and the thickness of the exposed and baked regions before and after development. No systematic variation in linewidth or thickness was evident with the introduction of 1 hour of PED. It is not clear whether the slightly rounded image profiles seen with SNR 248 are the result of acid deactivation at the resist surface or not. The acid deactivation by environmental contamination does not appear to be an issue with this chemistry.

Since ppb levels of basic vapors in the resist processing environment can profoundly effect the process performance of chemically amplified positive resists, solutions to this problem are required. IBM workers have shown excellent results by conducting the resist processing in an "amine (base) free environment" which was achieved by filtering air through activated charcoal filters [21].
We have concentrated our efforts in designing and synthesizing overcoat materials that are transparent and inert (at lithographically useful dose) to deep-UV radiation, sufficiently acidic such that they can quench airborne basic vapors and are aqueous base soluble. Aqueous base solubility is an important criterion as it simplifies the process sequence by allowing the removal of overcoat material during development. Aqueous base solubility of the overcoat also ensures complete removal of any intermixed material formed at the resist and overcoat interface.

Use of thin overcoat (300-2000Å) materials improved the resist sensitivity, dramatically alleviated the surface inhibition problems and improved the PED latitude [11]. No variation in linewidth, within experimental error, was observed up to at least 30 min (Fig. 5). We are in the process of testing the limits of PED latitude with several overcoat material.

![Fig. 5 SEM photomicrographs of 0.5 μm features of metal-ion free PTBSS resist formulation at PED = 1 and 15 mins.](image)

Use of overcoat materials does not necessarily preclude stringent control of the processing environment. In fact, the use of overcoat materials along with amine free environments should provide a much more robust and reproducible process. Introduction of an overcoat material does introduce an additional coating step in the process sequence. No additional intermediate soft-bake is necessary between the application of resist and overcoat.

![Fig. 6 Sensitivity vs PEB time and temperature for PTBSS resist formulations.](image)
Post-exposure Bake (PEB) Parameters

The PEB step is a critical process parameter since the dissolution selectivity is effected either through deblocking or crosslinking events during this step. Intel workers and others have shown that there exists a reciprocal relationship between the degree of crosslinking and PEB parameters (exposure dose, PEB time and temperature) in the case of SNR 248 [24]. It was also shown that PEB temperature affected the resist process most out of the three variables. A rather large activation energy of 40 kJ/mole was determined from an Arrhenius plot [25]. The large activation energy not only indicates that sensitivity can be manipulated by PEB parameters but also implies that small temperature variations across the wafer during postbake may not effect linewidth uniformity significantly. This is indeed the case and excellent linewidth uniformity (3σ < 10% CD) can be attained across the wafer [11].

Since the diffusion distance and the deprotection turnover rates are temperature dependent, one would expect dramatic improvements in resist sensitivity with increase in PEB temperature and time. This turns out to be the case with all covalent nitrobenzyl ester PAG base formulations we have examined. For example, a 6 mole % dinitrobenzyl tosylate formulation's sensitivity registered a 9 fold increase upon a 40°C increase in the PEB temperature (Fig. 6). A 50% increase in PEB time from 30 sec to 45 sec improved the sensitivity by 30-40%. While the trend is similar, the magnitude of the improvement is PAG molecular structure and loading dependent. Since the sensitivity is a strong function of PEB parameters, the sensitivity can be conveniently tuned to the process and exposure tool needs. The corollary of this might dictate tight control of PEB temperature for process reproducibility. However, a ±2°C temperature control and a ±5% bake time was found to be sufficient for process reproducibility. Excellent linewidth control (3σ < 10% CD) can be attained across the wafer [11].

Interestingly, the sensitivity of onium salt formulations do not exhibit such strong dependence on PEB parameters (Fig. 6). A 35°C increase in the PEB temperature did not alter clearing dose (D0) but surprisingly increased the linewidth of nominal 0.5µm features by ~20% (Fig. 7). Increasing the PEB time from 30 to 45 sec did not alter the D0 or 0.5µm linewidth.
The marked difference between covalent and $\text{Ph}_3\text{S}^+\text{AsF}_6$ formulations is puzzling and more mechanistic and analytical work is necessary to elucidate the differences in lithographic behavior. The high acid strength and volatility of $\text{HAsF}_6$, photoproduct of $\text{Ph}_3\text{S}^+\text{AsF}_6$, may explain the observed decrease in space widths with increased PEB temperature.

Development

The time elapsed between PEB and development (pre-development time delay) did not effect the positive or negative acting chemically amplified resist systems. In positive acting systems, the unexposed resist is insoluble whereas exposed and baked regions are extremely soluble in aqueous base. The liberation of phenolic or carboxylic groups during the PEB affords the polymer base solubility and the development of the exposed areas is complete within 10-15 secs. Development proceeds as a step function and greater than 95% t-Boc removal is necessary in PTBSS for base solubility [10].

The development step was the most forgiving and least critical process parameter of all in the positive resists we have evaluated and should be a general and very appealing feature of all chemically amplified positive resists based on deblocking chemistry. We have shown that as much as 2 fold variation in development concentration and 20 fold variation in development time has no effect on the process performance [10].

![Fig. 7](image1.png) ![Fig. 8](image2.png)

**Fig. 7** Linewidth of nominal 0.5 $\mu$m lines in line/space pairs as function of PEB temperature in PTBSS resist with $\text{Ph}_3\text{S}^+\text{AsF}_6$ PAG.

**Fig. 8** Swing curves for PTBSS resists with onium salt and nitrobenzyl ester PAGs.
In chemically amplified negative resist systems, both the unexposed as well as exposed and crosslinked areas are aqueous base soluble but the solubility rates of the exposed areas needs to be only a fraction of the unexposed region to attain high contrast and resolution. Because of the finite solubility of both the exposed as well as unexposed regions in the developer, developer concentration, time and temperature, as well as type of development (immersion, spray etc.) effect process performance and reproducibility [7,14].

**Thin film Interference Effects**

Adoption of a highly transparent base resin is essential in chemical amplification schemes to effect chemical reaction through the entire thickness of the resist film. Since the objective is to formulate an extremely sensitive resist, it is necessary to use as few photons as possible. Consequently, very few chemical events occur during the exposure, even with the assumption of a quantum yield of 1. Additionally, there is little change in the transmission spectrum of the resist at lithographically useful doses [7,10]. Lack of bleaching during exposure coupled with the higher reflectivity of substrates at 248 nm than at 365 nm or 436 nm (Table I) and the narrow band nature of excimer laser exposure exacerbates the reflectivity issue which in turn leads to a loss in CD control especially over topography [10,14,15,26].

**TABLE I.** Substrate Reflectivities at Different Imaging Wavelengths.

<table>
<thead>
<tr>
<th>Substrate</th>
<th>G-Line (@436 nm)</th>
<th>I-Line (@365 nm)</th>
<th>KrF Excimer Laser (@248 nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Poly Si</td>
<td>0.47</td>
<td>0.46</td>
<td>0.57</td>
</tr>
<tr>
<td>Nitride</td>
<td>0.49</td>
<td>0.34</td>
<td>0.59</td>
</tr>
<tr>
<td>Oxide</td>
<td>0.039</td>
<td>0.31</td>
<td>0.41</td>
</tr>
<tr>
<td>Aluminum</td>
<td>0.98</td>
<td>0.98</td>
<td>0.98</td>
</tr>
</tbody>
</table>

We have generated swing curves by determining $D_o$ as well as linewidth (at constant dose and focus) and plotting them as a function of resist thickness for both onium salt and nitrobenzyl ester PAG formulations with and without anti-reflection coatings. The amplitude of the swing curve measured for 0.5 $\mu$m nominal linewidth was slightly smaller (0.15 $\mu$m) for nitrobenzyl ester formulation than for an arsenate onium salt formulation (0.21 $\mu$m) (Fig. 8). The nitrobenzyl ester formulation has an absorption of 0.28/μm at 248 nm compared to the 0.24/μm absorption of the arsenate onium salt resist. The amplitude of the swing curve for 0.5 $\mu$m linewidth with SNR 248
was 0.18 µm. The period of the swing curve was ~740 Å and corresponds closely to the theoretical value of 830 Å calculated from λ/2n assuming a refractive index of 1.50 for PTBSS at 248 nm. The period of the swing curve was ~700Å for SNR 248.

Large amplitudes of the swing curve for essentially all reported chemically amplified resists necessitates thickness uniformities across a wafer better than 3 σ <25Å and thickness range smaller than 50 Å for acceptable CD control. While these specifications and hence good CD (<10% CD) uniformity are demonstrated on flat substrates (even with hand dispense of the resist !) [11]. It would be difficult to reproduce the same performance on device levels because of the thickness variations in resist as well as reflection from the underlying topography (Fig. 9) [10].

The amplitude of the swing curve can be significantly reduced by the use of thin, highly absorbing AR coatings underneath the resist layer [14,15,26]. Use of AR coatings, however, decreases the resist sensitivity. The AR coating system should not only intermix with the resist but should also be devoid of bases for use with chemically amplified resists. Small amounts of amines or bases in AR coating can detrimentally effect the resist sensitivity of both positive and negative materials and degrade image quality.

Processing of PTBSS formulations with AR coating materials reduced the amplitude of CD swing curve by ~4 times to about 0.05µm and provided acceptable CD control over topography without effecting the pattern profile (Fig. 10). The use of an AR coating, while introducing some complexity to the process, also alleviates the adhesion problems for positive resists and strippability issues for negative resists.
The use of AR coatings reduced the amplitude of swing curve from 0.18 to 0.04 µm in negative acting systems as well but the pattern profiles were considerably more retrograde [14,15]. The foot of the resist is thinner when an AR coating is used because of the reduction in the light reflected from the substrate which in turn reduces the extent of crosslinking. The need to overexpose features (lines) to prevent the adhesion failure of outermost lines in a line/space stack might be a limitation [14].

Faithful transfer of a resist pattern into the AR coating is a non trivial issue as it requires anisotropic etching of the AR coating which is further complicated by the variation in the thickness of AR coating due to underlying topography.

**Pattern Transfer**

Under appropriate plasma etching conditions, sub-0.5 µm features in PTBSS can be faithfully pattern transferred into substrates [10]. The etching rate of chemically amplified positive resist, however, varies with etching time (Fig. 11). The initial high etching rate observed in PTBSS formulations is probably the result of a PEB type of reaction occurring during etching, induced by heat and/or acid generated from the etching gases and from the exposure of material to the UV
emission of the plasma. After the initial thickness loss corresponding to the protecting groups, the etching rate of PTBSS resist is etching time independent and is actually lower than that of a conventional photoresist.

![Graph showing etching behavior of a PTBSS based chemically amplified resist and a conventional positive resist in a CHF₃ plasma.](image)

**Fig. 11** Etching behavior of a PTBSS based chemically amplified resist and a conventional positive resist in a CHF₃ plasma.

While pattern transfer can be achieved with positive chemically amplified resist systems, the resultant change in resist profile from the loss of protecting groups is a concern if not for process reproducibility issues, at least for aesthetic reasons. Design and synthesis of resist systems with smaller protecting groups and/or partially protected copolymers are some of the approaches we are currently pursuing to meet this goal.

The etching behavior of SNR 248 is similar to that of novolac resists. The severe retrograde profile on AR coating could be an issue during the pattern transfer.

**SUMMARY**

The chemistry and process performance of chemically amplified positive and negative resists capable of resolving sub-0.5 µm features with excellent sensitivity and good process control are discussed (Fig. 12). A comparison between the process performance of positive and negative acting chemically resist systems was provided and rationalized from the variation in the design of inherent chemistry.
The use of a positive resist is advantageous from the point of view of contact hole definition and development considerations, however, change in pattern profile during pattern transfer due to the protecting group removal does not seem to affect the process performance under optimized etching conditions. Design and synthesis of new materials with smaller protecting groups are some approaches toward achieving this. PED problems are alleviated with the applications of an overcoat but would mean an additional coating step in the process. No softbaking of the resist is necessary prior to the application of overcoat.

Negative resists based on acid catalyzed crosslinking chemistry are not subject to PED effects but are difficult to strip, provide little, if any, latitude for contact hole definition and result in retrograde profiles with AR coatings. Use of AR coatings favorably effects the stripping issue and mask bias may provide some latitude for definition of contact holes.

A lithographic strategy that would use positive and negative resists for different device levels may be a likely scenario.

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