# Preliminary Lithographic Characteristics of an All-organic Chemically Amplified Resist Formulation for Single Layer Deep-UV Lithography

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When used in conjunction with a nitrobenzylester photoacid generator, poly(t-butoxycarbonyloxy-styrene-sulfone) deep-UV resist films exhibit high contrast, good resolution and linewidth stability. Use of overcoat materials dramatically reduce the surface inhibition problems, improve the latent image stability (time delay) and enhance the sensitivity by isolating the resist surface from environmental contaminants that react with the photogenerated acid. The photospeed of the all organic CAMP formulation is lower compared to the arsenate based system but can be improved by using more aggressive PEB conditions. Coded, 0.35 μm l/s pairs could be resolved in 1 μm thick resist films at a dose of 20–30 mJ/cm$^2$. The exposure latitude is ~25% for 0.5 μm features, upon exposure with a GCA prototype deep-UV exposure tool with a NA = 0.35 and 5x reduction optics. This paper will discuss the resolution, depth-of-focus, exposure latitude and processing characteristics obtained during the evaluation of this chemically amplified resist.

## INTRODUCTION

New resist materials and processes must be developed in order to introduce deep-UV lithography into manufacturing[1]. The current conventional positive resist materials based on a novolac resin and diazonaphthoquinone dissolution inhibitors have limited use for the deep UV region (240-270 nm) due to their strong and non-bleachable absorbance. We recently reported a chemically amplified resist system comprised of a transparent, poly(t-butoxycarbonyloxystyrene-sulfone)[2] (TBSS) copolymer resin (OD ~0.1/μm) and triphenylsulfonium hexafluoroarsenate as the photo-acid-generator (PAG) which demonstrated 0.35μm resolution in 1μm thick films at a dose of 10 mJ/cm$^2$. While this resist exhibits

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good process latitude, its performance is critically dependent on controlling the elapsed time between the exposure and post-exposure bake (PEB) steps (post-exposure time delay). In addition, the presence of arsenic, a potential device contaminant, in the PAG may limit its acceptance by industry, especially as metal-ion free resist formulations become available.

The chemistry and preliminary lithographic characteristics of chemically amplified resist formulations consisting of metal ion free, non-ionic and non-volatile PAG materials has been reported[3]. These PAG materials are structural variants of 2,6-dinitrobenzyl tosylate and have been shown to be effective acid generators upon deep-UV irradiation. The photogenerated benzene sulfonic acids are sufficiently strong to effect the deblocking of the tert-butoxycarbonyl (t-boc) group significantly below the $T_g$ (glass transition temperature) of the matrix polymer, and hence are practical alternatives for onium salt resist formulations for chemically amplified systems based on t-boc deprotection chemistry. This paper reports the development efforts in the evolution of an organic PAG based chemically amplified positive resist formulation (CAMP) and process as well as its current capabilities.

## EXPERIMENTAL

### Materials preparation

TBSS copolymers were prepared from tert-butoxycarbonyloxystyrene and sulfur dioxide using a thermally induced free-radical polymerization employing AIBN (2,2'-azo-bis-isobutyronitrile) as the free radical initiator[4]. The organic PAG materials were synthesized as previously reported[3] and were evaluated for their photospeed, process latitude, thermal stability and shelf life.

### Materials characterization

The structure, composition and molecular properties of the polymers and PAGs were determined by a variety of analytical techniques that include elemental analysis, SEC (size exclusion chromatography), IR, $^{13}C$ and $^{1}H$ NMR spectroscopy, X-ray fluorescence measurements, and viscometry.

### Lithography

The resist solutions were prepared by dissolving the matrix polymer, TBSS, (10-20 wt%) and the appropriate amount of PAG, in a spinning solvent and by subsequent filtration (3 times) through a stack of 1.0, 0.5 and 0.2 μm Teflon® filters. The resists were spin coated onto the substrates and prebaked on an SVG System 88 wafer track (at Murray Hill) or MTI FlexiFab track (at SEMATECH) with resultant 1μm thick films. The substrates were typically primed with hexamethyldisilazane (HMDS) prior to application of the resist in a Yield Engineering Systems, Inc. (YES) oven. The film thickness measurements were done using either a Nanospec/AFT microarea thickness gauge or a Dektak IIA stylus profilometer. A refractive index of 1.50 was used for measuring film thickness with the Nanospec.

The resist coated substrates were exposed to 248 nm radiation using a GCA LaserStep® prototype deep-UV exposure system with an NA=0.35 lens and 5X reduction optics. Post-exposure-bakes were

performed on either an SVG system 88 track, SSI System 150 track or a Brewer Science hotplate model CEE2000 at Murray Hill, or an MTI FlexiFab track at SEMATECH. The delay time between exposure and PEB was varied from 30 sec. to 30 mins, and linewidth data was used to characterize the delay effects.

Development was done in the dip mode using 0.17 N tetramethyl ammonium hydroxide (TMAH) prepared by diluting commercially available 25% TMAH (Fluka, Inc.) with deionized water (1:15). The development time was typically 30 sec. Resist sensitivity is defined as the dose at which the resist completely clears.

Optical inspection of the developed images was done using a Reichert-Jung microscope. Resolution and image quality were determined by examining the gold coated resist profiles with a JEOL Model 35CFS SEM or carbon coated samples on an Amray model 1830 SEM. Linewidth measurements were done using a low voltage Hitachi model S6000 SEM.

## RESULTS & DISCUSSION

### PAG selection

Metal-ion free (organic) onium salts as well as non-ionic organic PAG materials were synthesized and evaluated using TBSS as the matrix resin using the process sequence given in Table I. Several PAG materials were evaluated in conjunction with the TBSS matrix polymer for photospeed, resolution and shelf-life. Onium salts typically possess higher thermal stability and are more effective deblocking agents as judged by the sensitivity data. This is not surprising, since the strengths of the acids, (e.g., triflic acid, $HAsF_6$ etc.) generated from the photolysis of onium salts are very high. While the sensitivity exhibited by these materials was excellent, they were extremely sensitive to time delay effects and exhibited poor process latitude. Nitrobenzyl ester based materials were also evaluated in conjunction with TBSS. Resist formulations utilizing such PAGS (~6 mole %) allow resolution of sub-micron patterns in 1μm thick films with good process latitude. The thermal stability of organic PAGS is >170°C and approaches that of onium salts.[5]

### Polymer molecular properties

The effect of copolymer molecular weight and composition (t–butoxycarbonyloxystyrene:$SO_2$) on resist sensitivity, resolution and contrast was previously examined using triphenylsulfonium hexafluoroarsenate as the PAG[6]. Similar results were obtained with the organic photoacid generator. Specifically, improved resolution was observed when the (t–butoxycarbonyloxystyrene:$SO_2$) ratio was >2.5:1 and the weight average molecular weight was <300,000. Process optimization was undertaken with TBSS copolymers of 100,000-150,000 molecular weight and 3:1 (TBS:$SO_2$) composition.

## Lithographic Performance

### Surface inhibition effects

A preliminary lithographic evaluation of resist formulations, irrespective of the organic PAG used, resulted in "T" shaped images and problems associated with surface residues that are insoluble in aqueous base developers were evident (Figure 1). It is postulated that these images are the result of "overexposure" that is required to clear trench patterns. Such overexposure, while aiding in breaking through the surface inhibition layer results in lines that are significantly smaller than the coded linewidths and contributes to adhesion problems and poor process latitude. These effects were found to be extremely dependent on the time delay between the exposure and PEB steps. This problem appears to be more severe for onium salt based formulations than for non-onium salt PAG based resists[2]. The maximum time delay available (defined as a 10% cd change) between exposure and PEB under optimum conditions was less than 3 minutes for 0.5 µm features. While this represents some improvement over what is available for the arsenate onium-salt resist system[2], it is insufficient to allow the design of a reproducible process.

Previously, it was shown that increased time delays result in incomplete deprotection of the t-boc functionality at the surface which results in the growth of a base-insoluble surface layer[2]. Presumably, reaction of the photogenerated acid with contaminants such as bases in the ambient atmosphere caused depletion of acid at the surface. Analysis of air samples indicated that the presence of as little as 15 ppb of a seemingly inocuous material such as HMDS (hexamethyldisilazane) in the ambient significantly affected image quality. Figure 2a depicts coded 0.5 and 0.45 µm patterns that were obtained in this HMDS contaminated atmosphere. Considering that the total concentration of acid generated in a 1µm resist film coated on a 5" substrate is only of the order of $10^{-5}$ to $10^{-6}$ mmol, and that 15 ppb HMDS can form several monolayers of material on the resist surface within seconds, it is conceivable that even such a small concentration of base in the ambient is capable of neutralizing some of the photogenerated acid. Since the turnover rates for deprotection are very high (~1000)[7], even a small decrease in acid concentration can cause a significant decrease in the extent of t-boc deprotection at the surface resulting in a base-insoluble (only partially deprotected) layer. Conducting the PEB in a less contaminated ambient (5 ppb of HMDS) enhanced the sensitivity by >50%, improved the line profiles and significantly reduced the surface inhibition effects (Figure 2b). While the process was more reproducible, resist performance was still dependent on immediate environmental conditions.

Since ppb base levels in the ambient can affect process performance profoundly, solutions to this problem are required. Some alternatives are:

1. Removal of the surface residue during development.
2. Addition of additives to the resist formulation designed to migrate to the surface to quench the basic contaminants in the ambient.
3. Performing resist processing in a very tightly controlled ambient.

4. Isolation of the resist surface from the ambient by means of application of an isolation layer (also called overcoat) on the top surface of the resist.

Experiments involving the addition of additives to the developer, or using more aggressive development conditions did not effect the removal of the surface residue. Process development under a tightly controlled ambient, while providing some control over the process, is probably less desirable than developing a forgiving process with the use of an overcoat. We have limited ourselves to water and base soluble polymeric materials for overcoat applications as this property allows the overcoat material to be removed during the development step and reduces process complexity. An additional spincoating step is, however, required.

Use of acidic copolymers as overcoats essentially eliminated the surface residue, enhanced the sensitivity by ~50% and dramatically improved the time delay latitude (Figure 3). No change was observed in linewidth even after a 15 minute time delay. This delay time is dependent on the thickness of the overcoat, and overcoat polymer composition and structure. The overcoat materials similarly improved the sensitivity and time delay latitude for CAMP resist formulations using other PAG materials, such as triphenylsulfonium hexafluorearsenate, triphenylsulfonium triflate and diphenyliodonium tresylate.

**Process Capability**

The current optimized resist formulation consists of 15-20 wt% of TBSS, 90,000-120,000 $M_w$ and 3:1 (TBS:$SO_2$) composition, and 6 mole % of a nitrobenzylester PAG material in EEP. The current optimized process sequence is listed in Table II.

*Thickness uniformity*

Thickness uniformity data was obtained by measuring various sites on the resist coated substrate with a nanospec. While, extensive data collection was not attempted, the limited data available does indicate that the thickness uniformity is typically between 15-30 Å (3 $\sigma$) with a typical thickness variation across the substrate being <50 Å. The results quoted for thickness uniformity were obtained with manual dispense of the resist and overcoat, and more uniform coatings are expected with auto dispense of the resist along with the use of currently available advanced tracks.

*Standing wave curve*

Standing wave curves[8] were generated on Si substrates by plotting sensitivity to clear large area patterns, and the linewidth of nominal 0.5 µm lines (at constant dose) as a function of resist thickness (Figure 4). The sensitivity varied from 16 to 20 dose units (1 dose unit ~0.9 $mJ/cm^2$) and the nominal 0.5 µm linewidth varied from 0.44 to 0.59 µm. The amplitude of the standing wave curve is lower than that obtained with the arsenate onium salt[2]. This effect is presumably the result of the higher absorbance (0.28/µm) of the organic PAG formulation.

*Resolution*

Rayleigh equations predict a minimum resolution in the range of 0.35 - 0.5 μm for a 0.35 NA le with 248.4 nm exposure light assuming a k value of 0.5 - 0.7.[9] Using the GCA prototype deep-U exposure tool, TBSS/PAG resist formulations are routinely capable of resolving coded 0.35 μm (line/space) patterns (Figure 5). Additionally, 0.4 μm windows could readily be resolved in 1.0 μ thick resist films. Preliminary data suggests that the resolution achieved to date in the chemica amplified resist discussed here is most likely exposure tool limited.

*Linewidth control*

Exposure and focus latitude are key elements that determine feature size and linewidth control images printed on a device substrate. Typically, broad tolerances are desirable to ensure a robust a reproducible process. The exposure latitude for a ±10% change in linewidth of a 0.5 μm line in line/space pair is estimated to be ±13%. The effect of defocus on linewidth is presented in Figure 6 a the defocus tolerance is defined for linewidth variations of ± 10% cd control. The total focal tolera for a nominal 0.5 μm line in a line/space pattern under optimum exposure conditions is about 1.5 μm.

The linewidth uniformity data for nominal 0.5 μm features were obtained by random measurem of 20 sites across a wafer. The 3 sigma variation was found to be below 0.05 μm for features printec both dark and bright fields.

*Thermal stability*

Post-development image thermal stability is a required property for any materials used in dev manufacturing. Clearly, developed resist images must be stable under the wide variety of processes t are used to transfer a resist pattern into the underlying substrate. In the case of the chemically amplif resist discussed here, the Tg (glass transition temperature) of TBSS is ~165°C and the polymer itsel thermally stable up to ~175°C. DSC (differential scanning calorimetry) and TGA(thermogravime analysis) studies of the nitrobentyl ester PAG indicate that in crystalline form, it is stable up to 200 The images were found to be thermally stable up to 140°C.

## SUMMARY

Organic PAG based CAMP formulations in EEP exhibit high contrast, good resolution linewidth stability with the use of a thin overcoat. Use of acidic overcoat materials dramatically redu the surface inhibition problems, improved the latent image stability (time delay) and enhanced the se tivity by isolating the resist surface from environmental contaminants that react with the photogenera acid. The photospeed of the all organic CAMP formulations is lower compared to the arsenate ba system but can be improved by using more aggressive PEB conditions. The exposure and developm response of the organic PAG and onium salt PAG based systems are essentially the same.

Efforts are currently underway to further optimize the resist formulation with respect to resist overcoat copolymer molecular properties and PAG concentration to achieve better photospeed, adhe:

and thermal stability. We are also in the process of determining the latitude of the current process.

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**Table I: Deep-UV Chemically Amplified Resist Process Sequence**

| | |
|---|---|
| Spin coat | Nominal 1μm film |
| Prebake | 105° C/2mins |
| Exposure | 1-200 mJ/cm$^2$ |
| Exposure Delay | 30 sec |
| Post Exposure Bake | 115° C/30 sec |
| Development Delay | None |
| Development | 30 sec in 0.17 N TMAH |
| Rinse | 20 sec in $H_20$ |

**Table II: Process Sequence for CAMP Material**

| | |
|---|---|
| Resist Application | 3000-4000 rpm for nominal 1 μm film |
| Prebake | 105°C / 45 sec |
| Overcoat Application | 3000 rpm |
| Rebake | 105°C / 45 sec |
| Exposure | 50-70 mJ/cm$^2$ |
| Exposure Delay | 30 sec |
| Post Exposure Bake | 115°C / 30 sec |
| Development Delay | None |
| Development | 30 sec in 0.17 N TMAH |
| Rinse | 20 sec in $H_2O$ |

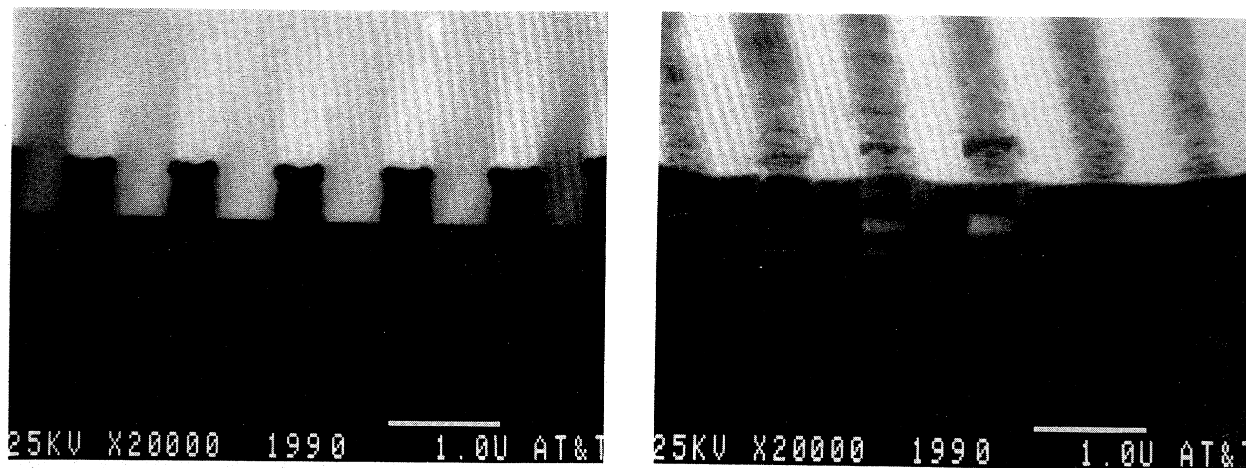
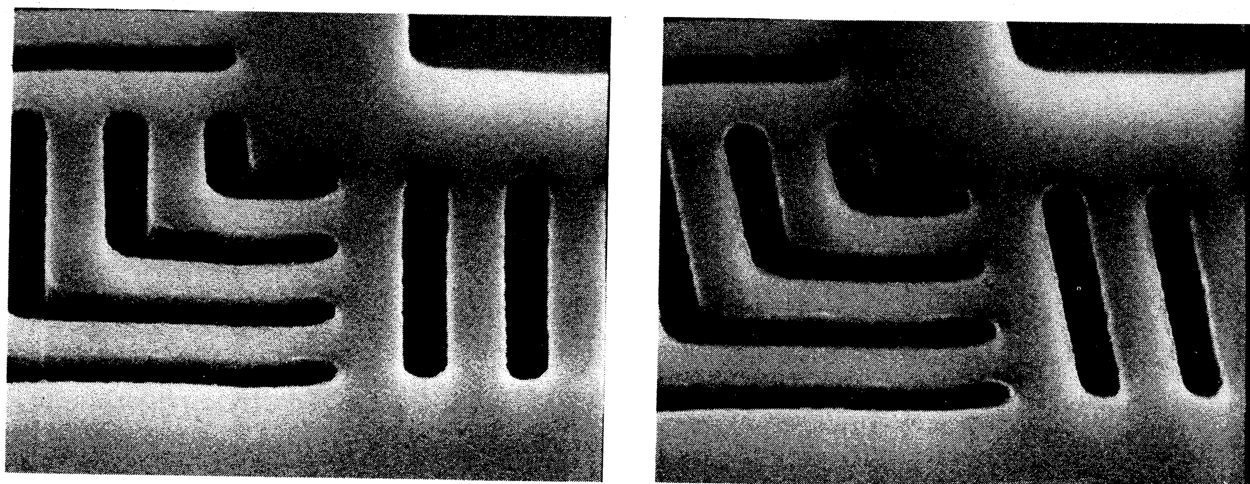



Figure 1. Representative SEM micrographs depicting coded 0.5 μm line/space patterns obtained in a 1.0 μm thick TBSS/PAG formulation.

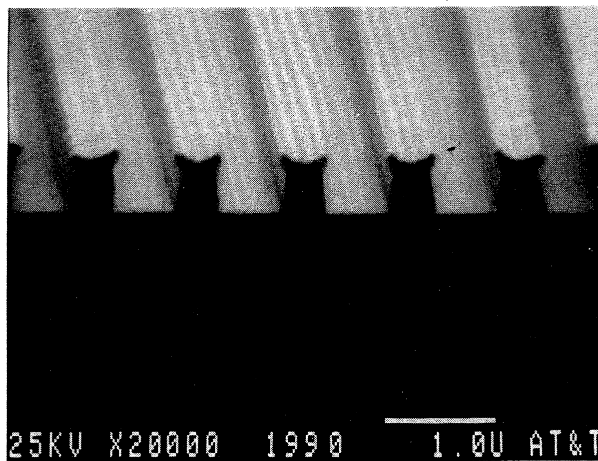


**0.5 μm**

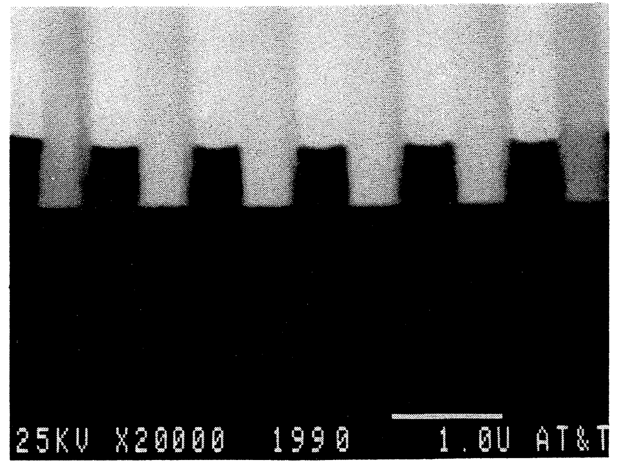
**(a)**
**1 min. time delay**

**(b)**
**15 min. time delay**

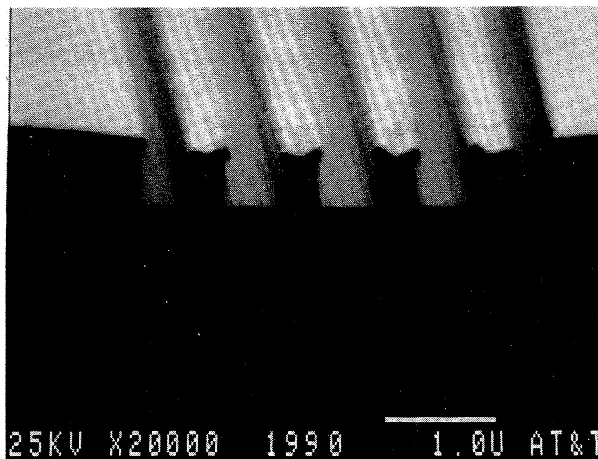
Figure 3. SEM micropraphs depicting coded 0.5 μm features obtained in TBSS/PAG resist formulations after a) a 1 minute time delay and b) a 15 minute time delay using an overcoat material.



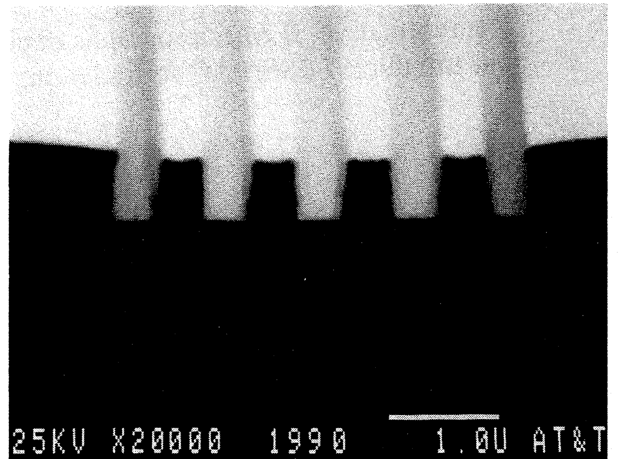

0.5 $\mu$m




0.5 $\mu$m




0.45 $\mu$m




0.45 $\mu$m

**(a)**
**HMDS-Rich Environment**

**(b)**
**HMDS-Poor Environment**

Figure 2. SEM micrographs depicting coded 0.5 and 0.45 μm line/space patterns obtained in a 1.0 μm thick TBSS/PAG resist formulaton in a) an HMDS contaminated atmosphere and b) an HMDS "free" atmosphere.

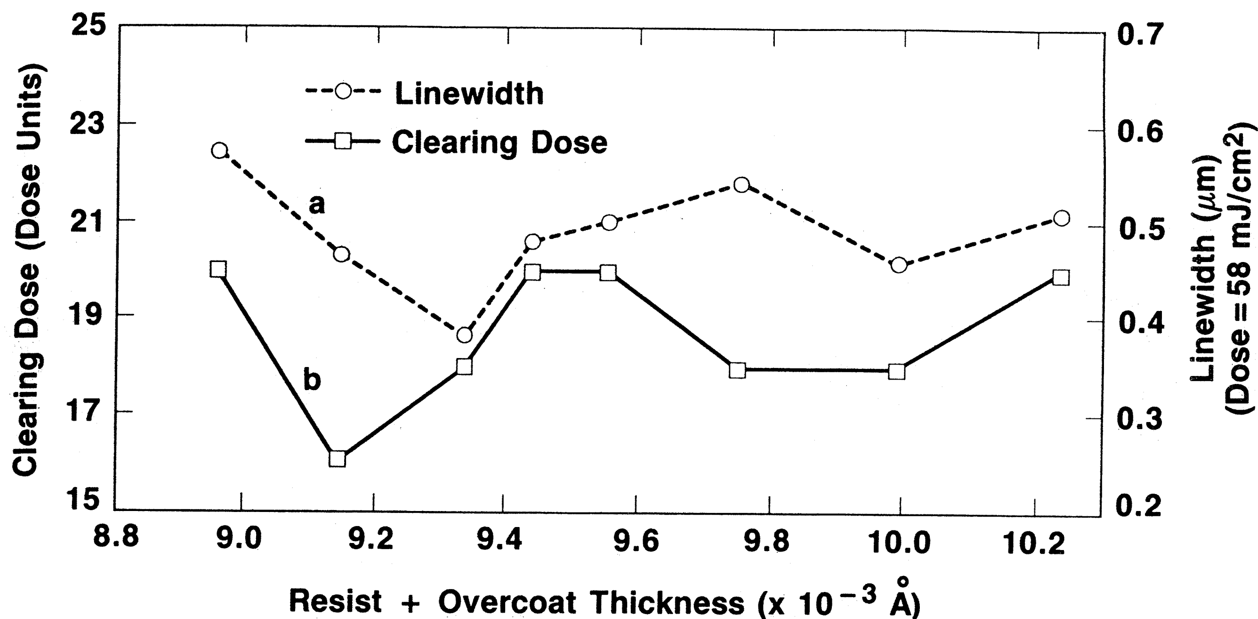



Figure 4. Plot of a) 0.5 μm linewidth and b) clearing dose vs. resist and overcoat thickness for a TBSS/PAG resist formulation.

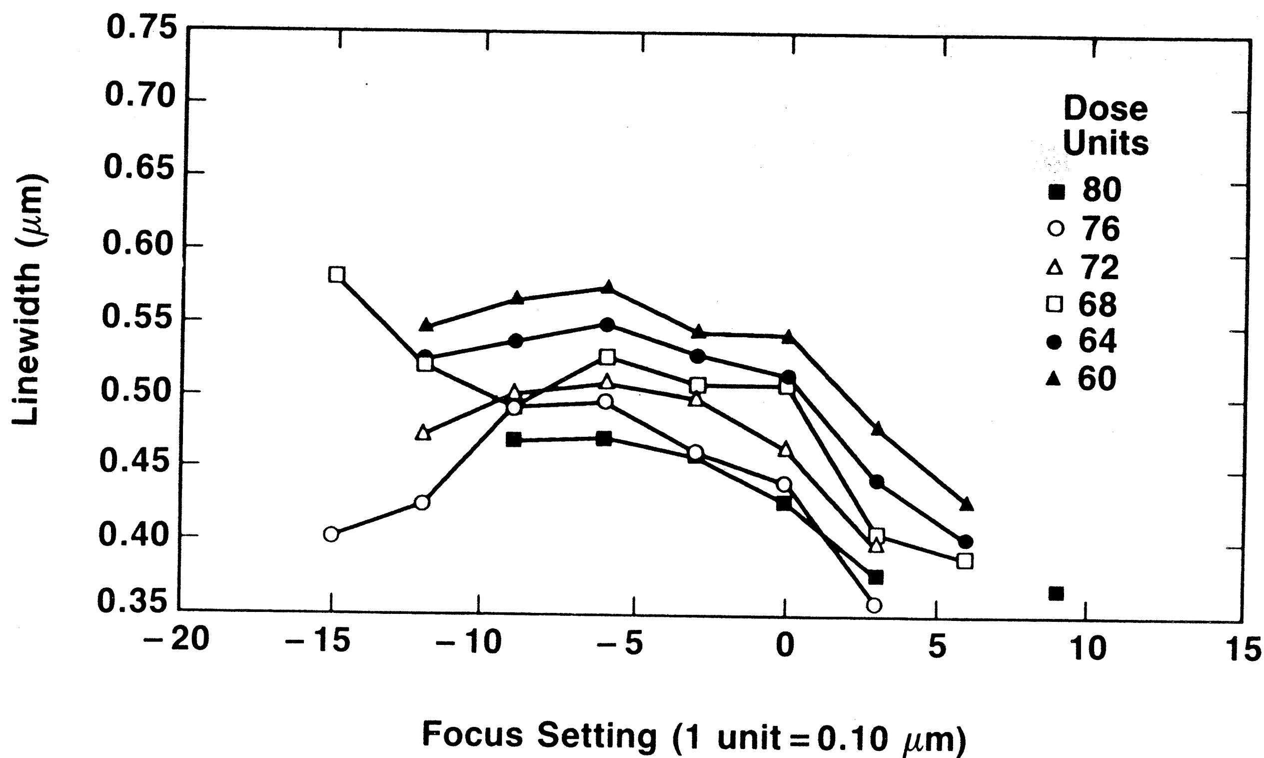



Figure 6. A typical plot of focus setting vs. linewidth for 0.5 μm features obtained in a TBSS/PAG resist formulation using an overcoat material.

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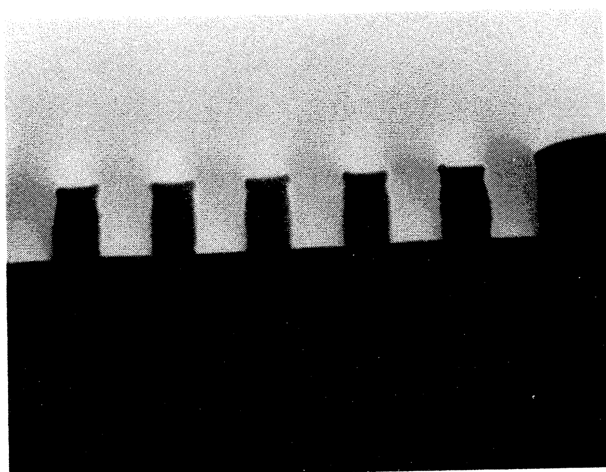
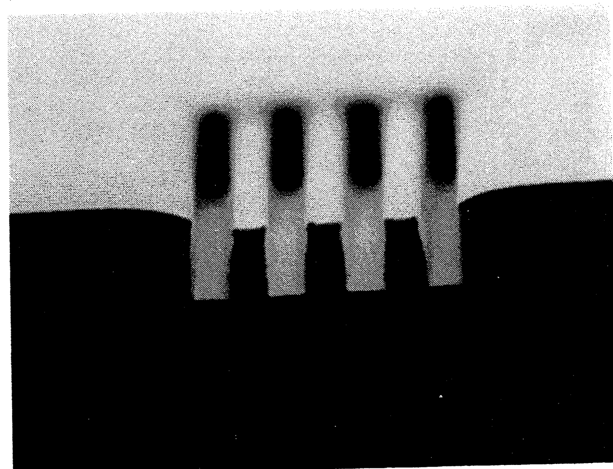
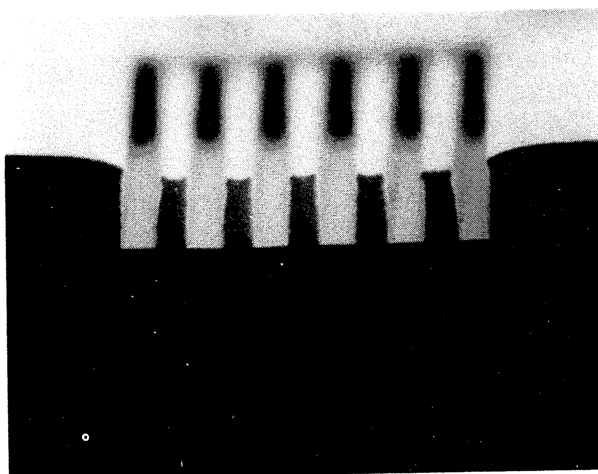


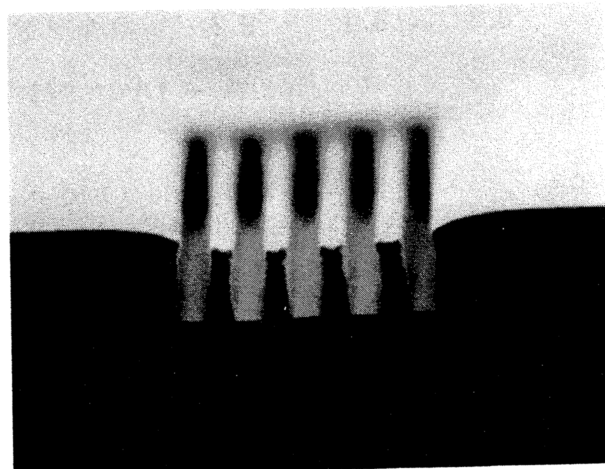
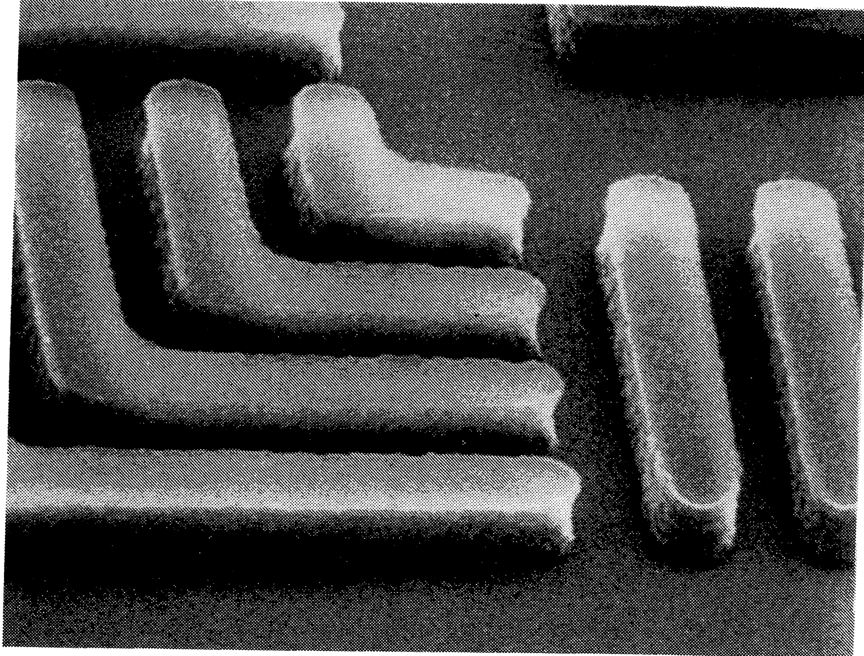
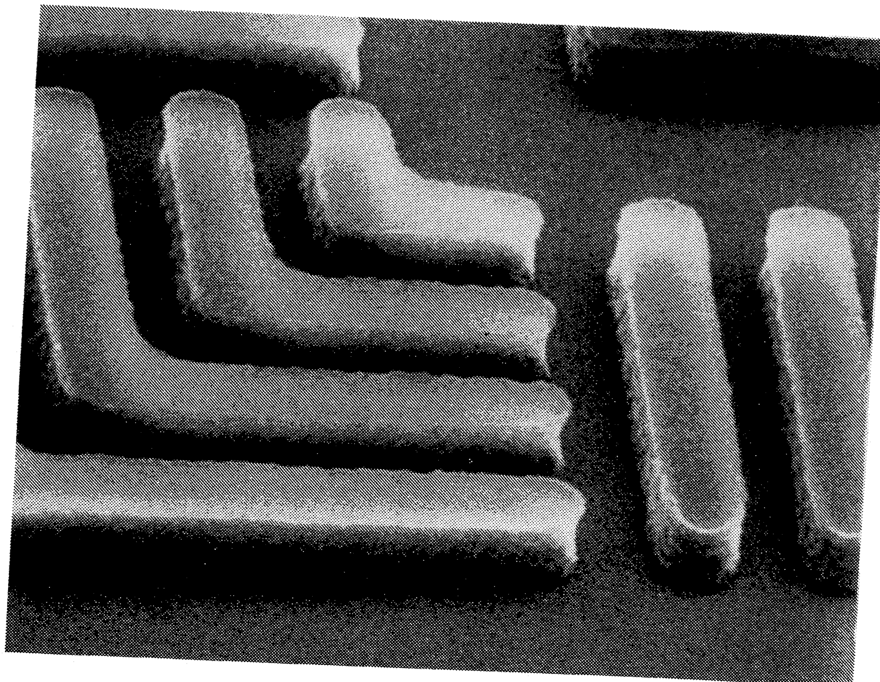




Figure 5. SEM micrographs depicting coded a) 0.50 μm, b) 0.40 μm, c) 0.35 μm, d) 0.30 μm line/space patterns obtained in a dark field and e) 0.5 μm line/space patterned obtained in a bright field using a TBSS/PAG resist formulation.



**5e**



**5e**