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PAG Segregation During Exposure Affecting Innate Material Roughness[*]

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ABSTRACT

We have developed an improved AFM-based technique to measure intrinsic material roughness (IMR) after base development. We have investigated the contribution of different polymeric PAGs to IMR. These polymeric PAGs include copolymers of several styrenic PAGs with hydroxystyrene. The IMR of these polymer-bound PAGs is reduced relative to that of their nonpolymeric counterparts with DUV exposure. Theses results represent further evidence for PAG segregation during the bake steps as being responsible for increased IMR in exposed resists, presumably by increasing the dissolution rate inhomogeneity on a nano-scale level. The work also shows that the effects of PAG segregation can be mitigated by employing polymer-bound PAGs.

Keywords: Photoresist, linewidth roughness, PAG, polymer

1. INTRODUCTION

Characterizing the relationship of resist materials to line edge roughness (LER) through a systematic study represents an opportunity to reduce the degree of line width roughness (LWR). Unfortunately, the ability to do a systematic study of this relationship is limited in many cases by the nature of the relationship. Any systematic study that changes the resist material must also affect the resist contrast and thus lead to the issue that the material factor being studied influences the resist contrast, and hence LER, more than it influences the material roughness directly. It has been shown that attempts at a systematic study of resist materials have been hindered when certain combinations of materials produced resists that could not be studied due to poor imaging characteristics.[1] It therefore becomes necessary to remove the interplay of the resist contrast from the study of material contributions to image roughness.

In order to manifest any material differences into the final lithographic image, these material differences must be borne out in the development process. This was recognized in an investigation into factors contributing to LER where the development process was seen to be a major factor.[2] It was also reported that differences in the level of polymer deprotection can lead to distinct phase separated morphology and that surface roughness can be enhanced by the development process.[3] During the development process it was noted that the surface roughness was not constant in the resist, but depended on both the resist material and the amount of resist loss during the development process.[4]

Thus it is expected that the resist dissolution properties will be a key factor in the propensity of a given resist to be prone to LER. These dissolution properties are a clear function of the resist material and give rise to the speculation that each unique material has an intrinsic material roughness (IMR) that can be realized or partially suppressed during the development process. It would greatly improve resist understanding if factors that influence or control the IMR of a material can be understood.

Material aggregates may be the root cause of resist surface roughness and again presumably LER. It has been suggested that phase separation into polymer rich and polymer poor regions with differing development characteristics are responsible for material roughness in PMMA resists.[5] It has also been observed that annealing polymer blends leads to a pronounced increase in surface roughness due to some type of phase separation.[6] It was also reported that aggregate size is a function of polymer molecular weight.[7] These aggregates can also be due to PAG separation that would be a function of the polymer matrix.[8] The segregation of PAGs was supported by analysis of a variety of polymer and PAG combinations carried out by using Rutherford backscattering spectrometry.[9]

We have employed a technique called resist deconstruction to probe which material factors can also impact resist roughness.[10] This method involves performing a contrast curve and measuring the resulting film roughness with differing degrees of film lose. This technique allowed for the identification of the PAG as a major contributor to

IMR.[11,12] Further work identified the inhibition properties of the PAG coupled with PAG segregation during post exposure bake step as significant contributors of IMR and by inference of LWR.[13] A correlation between atomic force microscope (AFM) and chemical force microscope (CFM) responses provided direct evidence that PAG segregation occurred and that this segregation was responsible for the observed film surface roughness.[14] It was further shown that no linkage existed between resist sensitivity and IMR but instead a relationship exists between IMR and the PAG and polymer material properties.[15]

Some work called into question the exclusive dependence on shot noise as both a limiter and significant determinant of LWR. It was found that no simple relationship exists between IMR and sensitivity and instead some other, more complex relationship between the material properties of the polymer and resist process that is determining both the IMR and sensitivity. This suggests that resist performance is not innately limited by any fundamental law but is instead open to further improvements through the use of new materials or material combinations.[16]

One option to reduce the propensity of PAGs to segregate is to employ polymeric PAGs, whereby the PAGs is polymerized or copolymerized with monomers similar to those employed in the resist polymer. The PAGs can be considered to be either cation-bound, where the acid is liberated during exposure or anion-bound, where the photoacid remains attached to the polymer main chain. An early report of the synthesis and use of cation-bound PAGs showed that both PAG homopolymer and copolymers were capable of being employed in high sensitivity resists with little change in acid generation efficiency.[17] It was later shown that both anion-bound and cation-bound PAGs could be prepared and that cation-bound PAGs had increased sensitivity due to presumably higher rates of acid diffusion.[18] This work also noted that some degree of phase segregation occurred which could be explained by the choice of the more non-polar styrene as the second monomer.

In order to overcome the possibility of polymeric PAG phase segregation a series of cation-bound PAG terpolymers were prepared to mimic an ESCAP-like resist polymer incorporating less than 10% molar PAG. These polymer-bound PAGs were shown to be efficient acid generators.[19] Further work on both hydroxystyrene[20] and methacrylate[21] based terpolymers showed high resolution imaging with the promise of reduced LWR. This promise of reduced LWR led us to investigate several different cation-bound and anion-bound PAGs by our resist deconstruction methodology whereby film IMR was determined at various depths into developed resist for both monomeric and polymer-bound PAGs.

2. EXPERIMENTAL

The 65:20:15 poly(hydroxystyrene-co-styrene-co-t-butylacrylate) (Poly-J) and 66:20:10:4 poly(hydroxystyrene-co-styrene-co-t-butylacrylate-co-methacrylic acid) (Poly-K) polymers were obtained from DuPont Electronic Polymers. Tetrabutyl ammonium hydroxide (TBAH) was obtained from Aldrich Chemical.

Triphenylsulfonium salt 4-(vinyl)benzenesulfonate (VBS-TPS) was prepared by the method of Gonsalves by reacting sodium 4-styrenesulfonate and triphenylsulfonium chloride.[17] Triphenylsulfonium salt 4-(methacryloxy)benzenesulfonate (MBS-TPS) was likewise prepared by the method of Gonsalves by reacting sodium 4-phenosulfonate and metharylic acid.[19] Phenyl methacrylate-4-(dimethylsulfonium triflate) (PDMS-Tf) was prepared following the procedure of Gonsalves[17] by condensing phenol with dimethyl sulfoxide in the presence of dry hydrogen chloride to give dimethyl-4-hydroxyarylsulfonium chloride which was converted to the corresponding triflate salt. The sodium salt of the phenol was then reacted with methacryloyl chloride to give PDMS-Tf.

The TPS-VBS and TPS-MBS based polymers were prepared by free radical polymerization by heating a solution of monomers and ABIN in DMF at 65°C for 48 hours followed by precipitation in water. The polymer was dried under vacuum overnight at 30°C and the final polymer composition determined by NMR. The PDMS-Tf based polymers were prepared by free radical polymerization by heating a solution of monomers and ABIN in acetonitrile at 60°C for 48 hours followed by precipitation in THF. The polymer was dried under vacuum overnight at 30°C and the final polymer composition determined by NMR. The monomer feed ratio and final polymer compositions are shown in Table 1. The number after the polymer name refers to the weight percent of PAG monomer in the final polymer.

Table 1. Polymerization results for the preparation of polymeric PAGs with all values in mole percent.

Polymer Name	Monomer Feed Ratio			Polymer Composition	
	HOST	PAG	ABIN	HOST	PAG
P(TPS-VBS-32)	80	20	2.5	90	10
P(TPS-VBS-54)	50	50	4.1	76	24
P(TPS-MBS-36)	80	20	5.1	88	12
P(TPS-MBS-70)	50	50	3.7	64	36
P(PDMS-Tf-100)		100	7.6		100
P(PDMS-Tf-37)	80	20	3.0	84	16
P(PDMS-Tf-69)	50	50	4.6	58	42

All resists were formulated based on materials weight percent with 95% polymer, 5% PAG and 0.38% TBAH in DMSO solvent. Resists containing monomeric PAGs were formulated with 5% PAG and 95% of either 65:20:15 poly(hydroxystyrene-co-styrene-co-t-butylacrylate) or 66:20:10:4 poly(hydroxystyrene-co-styrene-co-t-butylacrylate-co-methacrylic acid). The polymeric PAG containing resists were formulated by adjusting the polymer and polymeric PAG content to have the weight percent of the PAG component in the resist equal to that of monomeric PAG resists. The polymeric PAG amounts are shown in Tables 2 and 3.

Dissolution rates were typically obtained by coating 250 nm of the material on a silicon wafer, baking at 130°C for 60 s, and determining the dissolution rate in LDD-26W with a Luzchem TFA 11. The surface roughness was determined on a Veeco Dimension 5000 AFM with scans performed in tapping mode on a 5 by 5 micrometer square area with 19.5 nm between sampling points. The RMS surface roughness was determined by Veeco analysis software. The IMR is determined by averaging all measured RMS values for film depths of greater than 50 nm.

All lithographic substrates were HMDS treated 6-inch silicon wafers. The 248-nm exposures employed an organic antireflection coating, Shipley AR3, which was coated to 62 nm on the silicon wafer, followed by a bake of 215°C for 60 seconds. All resists were coated to 250-nm and baked at 140°C for 60 seconds. Following exposure, the resist was baked for 90 seconds at temperatures of either 100 or 130°C. Development was by single puddle with Shipley LDD-26W for 40 seconds. All 248-nm exposures were with a Canon EX-4 248-nm 0.6 NA stepper.

3. RESULTS AND DISCUSSION

We are now extending our technique called resist deconstruction to probe the effect of polymeric PAGs on material roughness. In this technique the resist is broken down into component parts and then reassembled in controlled conditions with each individual component studied to determine its effect on material roughness. Previous work employing this technique identified PAG as a major contributor to intrinsic material roughness. We now employ this technique to study a series of monomeric and polymeric PAGs to determine the effect of polymer-bound PAGs on IMR.

Key to employing this technique is to obtain monomeric and polymeric PAGs that can be added to traditional resists polymers to directly compare any differences in dissolution rates or surface roughness attributed to PAG. Thus our focus was to not prepare polymeric PAGs in which the PAG was fully incorporated into the resist polymer in a single component PAG-polymer system, but to instead prepare polymeric PAGs in which the PAG was incorporated into a polymer that was fully compatible with traditional resist polymers. This requires that the resist polymer alone be responsible for dissolution switching and that the polymeric PAG be added at levels that do not greatly impart the dissolution switching of the resist polymer. An outcome of this requirement is that the polymeric PAG must contain a high weight percentage of the PAG component so as to validate comparison between monomeric and polymeric PAGs and effectively separate the impact of the non-PAG containing monomers contained within the polymeric PAG.

3.1. Preparation of polymeric PAGs

In order to explore the effect of PAG phase segregation on IMR a variety of polymeric PAGs were prepared. Several key PAG monomers were prepared according to literature procedures.[17, 19] The chemical structures of the PAG monomers employed in this study are shown in Figure 1. TPS-VBS is a styrenic based PAG that is capable of copolymerizing with styrene, acrylate, and methacrylate based monomers. TPS-MBS is an acrylate based PAG that is also capable of copolymerizing with styrene, acrylate, and methacrylate based monomers. Both PAG monomers share a common feature in that when polymerized they are anion-bound PAGs. Anion-bound PAGs are characterized by having the photogenerated acid covalently attached to the polymer backbone. This attachment is expected to hinder acid diffusion during resist thermal processing by effectively having a significantly larger acid molecule when compared to the corresponding monomer. This attachment also allows the non-acidic cation to diffuse unencumbered from the polymer.

A cation-bound PAG monomer was also prepared, PDMS-Tf, and the chemical structure is again shown in Figure 1. The cation-bound PAGs are characterized by having the photogenerated acid liberated from the polymer backbone during exposure and thus would be expected to have acid diffusion rates similar to that of the monomeric PAGs during resist thermal processing. This attachment would be expected to reduce the diffusion rate of the still polymer bound non-acidic anion relative to that of the corresponding monomeric PAG.
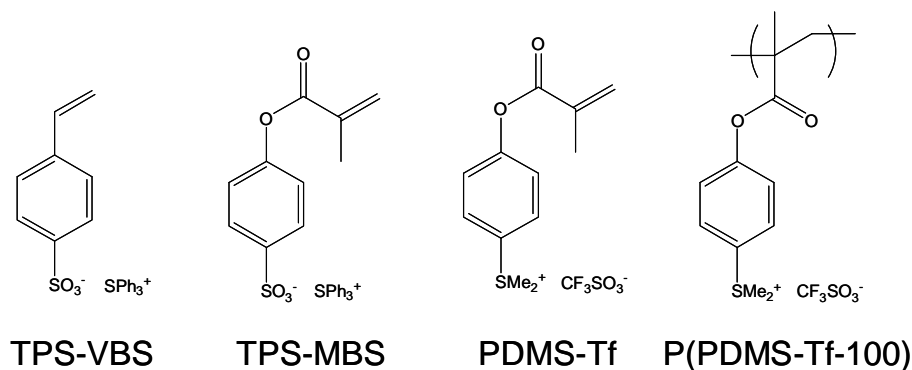

Figure 1. Chemical structures of PAG monomers and homopolymer.

Initial efforts were focused on the preparation of PAG homopolymers in which the PAG would be the only component present in the polymeric PAG. The homopolymer P(PDMS-Tf-100), structure shown in Table 1 was prepared from monomer PDMS-Tf following the procedure of Gonsalves.[17] Multiple attempts to prepare homopolymers of TPS-VBS and TPS-MBS by a similar or modified method yielded insoluble materials that were not further characterized. The inability to prepare the TPS-VBS and TPS-MBS homopolymers prompted us to prepare copolymers of TPS-VBS and TPS-MBS with hydroxystyrene.

Copolymers of both TPS-VBS and TPS-MBS with hydroxystyrene were prepared successfully employing conditions described in the experimental section. The goal of this synthesis was to prepare PAG copolymer containing relatively high amounts of PAG monomer. Toward that goal, the molar monomer feed ratios were set at 80:20 and 50:50 (hydroxystyrene:PAG monomer). The synthesis of TPS-VBS and TPS-MBS copolymers with hydroxystyrene was successful although as Table 1 shows, the final molar monomer ratios as roughly half of that expected from the initial monomer feed.

Figure 2 shows the chemical structures of the TPS-VBS and TPS-MBS copolymers. It is noted that the abbreviated names chosen for these copolymers reflect the weight percent of PAG monomer present in the copolymer. As an example P(TPS-MBS-70) contains 70 weight percent TPS-MBS. Although these four PAG containing copolymers contain only 10 to 36 molar percent of PAG, the higher molecular weight of the PAG monomer relative to that of hydroxystyrene means that the weight percent of PAG in these copolymers range from 32 to 70 weight percent. We have thus met our goal of preparing solvent soluble PAG containing copolymers with high weigh percents of the PAG monomer.

P(TPS-VBS-32)   P(TPS-MBS-36)   P(PDMS-Tf-37)
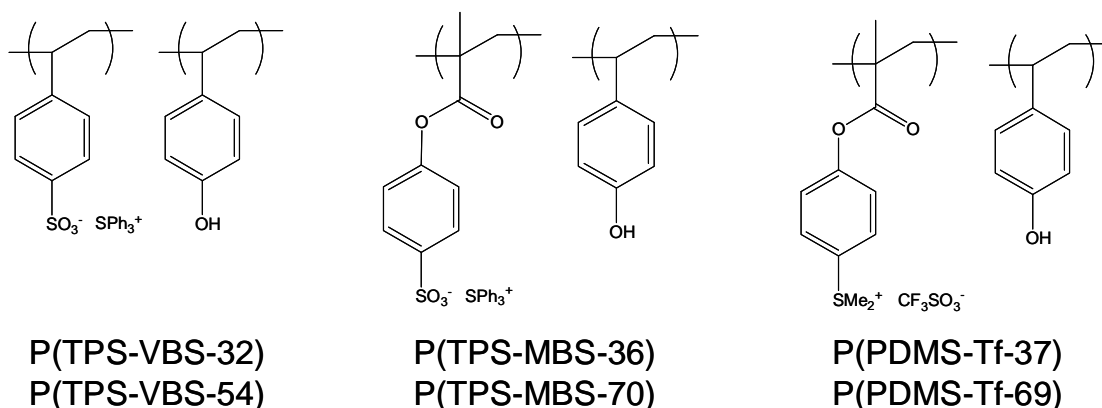P(TPS-VBS-54)   P(TPS-MBS-70)   P(PDMS-Tf-69)

Figure 2. Chemical structures of PAG copolymers. Monomer ratios are shown in Table 1.

Copolymers of PDMS-Tf with hydroxystyrene were also successfully prepared employing conditions described in the experimental section and Figure 2 again shows their chemical structures. The PDMS-Tf containing hydroxystyrene copolymers had their molar monomer feed ratios set at 80:20 and 50:50 (hydroxystyrene:PAG monomer) and had final molar monomer ratios of either 84:16 or 58:42, amounts only slightly less than the initial monomer feed. Thus the final PAG weight percent of the PDMS-Tf containing hydroxystyrene copolymers was 37 and 69 weight percent. The comparable weight percent PAG of these copolymers, even with the higher molar PAG ratio, relative to the TPS-VBS and TPS-MBS copolymers is a reflection of the higher molecular weight of the TPS-VBS and TPS-MBS monomer relative to that of the PDMS-Tf monomer.

3.2. Polymeric PAG IMR without exposure or thermal deprotection

It is expected that the resist dissolution properties will be a key factor in the propensity of a given resist to be prone to LER. These dissolution properties are a clear function of the resist material and have given rise to the speculation that each unique material has an intrinsic material roughness that can be realized or partially suppressed during the development process. We employed a previously developed AFM-based technique to measure intrinsic material roughness after base development. This method involves performing an interrupted development of the resist film and after a certain fixed film loss, measuring the resulting film roughness. Experimentally, we have found that all classes of phenol-based materials that we have studied reach a terminal material roughness (TMR) that can be considered the IMR after 50 nm of material loss. This IMR represents the intrinsic material roughness and is unique for different phenol-based materials.

In deconstructing the resist, it is first necessary to identify the key component parts and how those parts can first be separated and then reformulated as required. This requires that both an initially protected starting polymer as well as a partially deprotected polymer be available. As previous work had identified the PAG as the major contributor to IMR, we concentrated on determining the effect of monomeric and polymeric PAGs on IMR in both a fully and partially protected resist polymer.

The two polymers employed in this study are called Poly-J and Poly-K and their chemical structures are shown in Figure 3. Poly-J is a typical ESCAP-type terpolymer employed in many advanced DUV and EUV resists. Poly-K was prepared to mimic the expected acid catalyzed thermal deprotection product of Poly-J with some of the t-butyl acrylate replaced by acrylic acid. Poly-J was previously shown to have a minimal base dissolution rate of 2.4 nm/s[10], Poly-K has an order of magnitude higher dissolution rate in base developer as seen in Table 2. In order to determine the effect of monomeric and polymeric PAGs on IMR without exposure and bake a series of resists were prepared based on Poly-K and the IMR with base development determined.
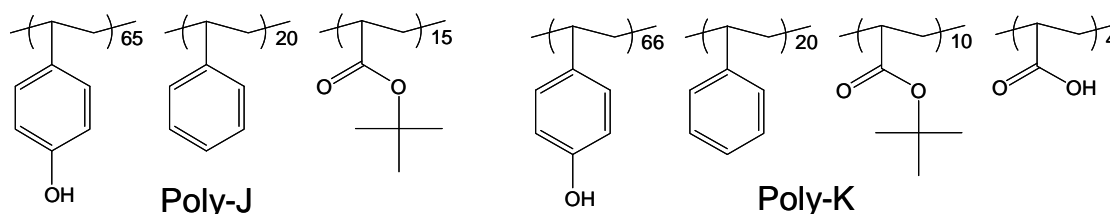
Figure 3. Chemical structures of non-PAG containing polymers.

The dissolution characteristics of resists containing both monomeric and polymeric PAGs are shown in Table 2. Resists were formulated with Poly-K and 5 weight percent PAG for monomeric PAGs and for polymeric PAGs, the weight percent shown in Table 2 which is equivalent to 5 weight percent PAG based on the weight of PAG in the polymeric PAG. It can been seen, from Table 2, that both TPS-VBS and TPS-MBS are dissolution inhibitors in that the dissolution rate of Poly-K is reduced to less than 1.0 nm/s. The polymeric PAGs derived from TPS-VBS and TPS-MBS are likewise dissolution inhibitors with the dissolution rate ranging from 0.7 to 4.3 nm/s and the degree of dissolution inhibition is in a rough direct relationship to the weight percent of PAG in the copolymer. In contrast, the PDMS-Tf monomer, homopolymer, and hydroxystyrene copolymers have little effect on the film dissolution rate relative to Poly-K with dissolution rates ranging from 24.9 to 34.0 nm/s for PAG containing films as compared to 28.2 nm/s for the Poly-K. These PAGs are either dissolution rate neutral or possible slightly dissolution rate accelerating.

Table 2. Summary of IMR for resists with various PAGs without exposure.

Resist	PAG	PAG Amount (%)	Dissolution Rate (nm/s)	IMR (nm)
Poly-K1	none	None	28.2	1.6
LUVR-99387	TPS-VBS	5.0	0.9	2.8
LUVR-99388	P(TPS-VBS-32)	16.6	4.3	8.8
LUVR-99389	P(TPS-VBS-54)	9.2	0.7	6.9
LUVR-99390	TPS-MBS	5.0	0.9	2.5
LUVR-99391	P(TPS-MBS-36)	15.0	1.4	8.4
LUVR-99392	P(TPS-MBS-70)	7.4	0.8	4.6
LUVR-99425	PDMS-Tf	5.0	31.5	1.8
LUVR-99426	P(PDMS-Tf-100)	5.0	24.9	2.2
LUVR-99427	P(PDMS-Tf-37)	13.5	34.0	3.7
LUVR-99428	P(PDMS-Tf-69)	7.3	31.0	1.9

An example of the AFM-measured surface roughness as a function of developed depth into Poly-K films containing the three monomeric PAGs is shown in Figure 4. All films have an initial RMS roughness of less than 0.4 nm (approaching the limit of the AFM) and quickly rise over the first 20 to 30 nm to a near constant value which we call the IMR. The IMR values for these three resists are shown in Table 2 where the IMR values are all relatively low with the dissolution rate inhibiting PAGs, TPS-VBS and TPS-MBS, having higher IMR than PDMS-Tf.

A comparison of the surface roughness versus developed depth of Poly-K films containing either TPS-VBS or its polymeric analog is shown in Figure 5 and a similar comparison of Poly-K films containing either TPS-MBS or its polymeric analog is shown in Figure 6. Figure 5 shows that films containing either P(TPS-VBS-32) or P(TPS-VBS-54) exhibit considerably higher RMS surface roughness than the monomeric TPS-VBS with the higher hydroxystyrene containing copolymer having a higher IMR as shown in Table 2. A similar effect is observed in Figure 6 for the P(TPS-MBS-36) and P(TPS-MBS-70) containing films when compared to that of the monomeric TPS-MBS. Again the polymeric PAG containing films exhibit higher RMS surface roughness than the monomeric TPS-MBS with again the higher hydroxystyrene containing copolymer having a higher IMR as shown in Table 2.
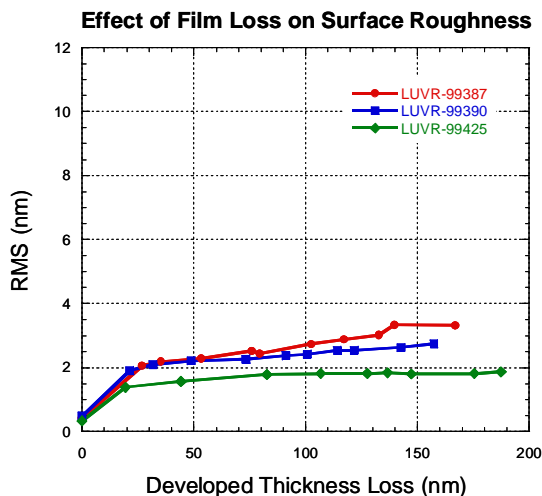
Effect of Film Loss on Surface Roughness

Figure 4. Depth profiling of film roughness for films containing monomeric PAG and Poly-K.

Effect of Film Loss on Surface Roughness
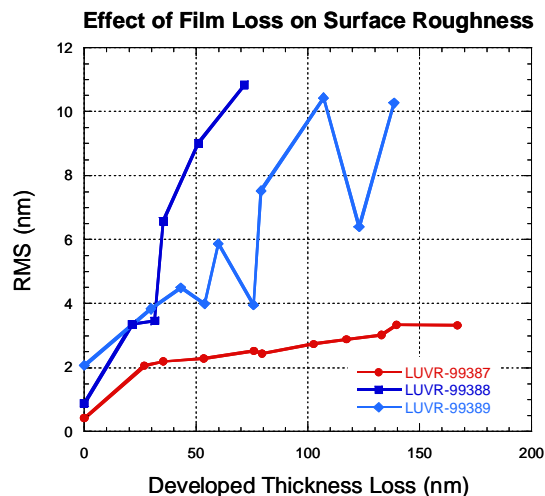
Figure 5. Depth profiling of film roughness for films containing TPS-VBS based PAG and Poly-K.

Effect of Film Loss on Surface Roughness
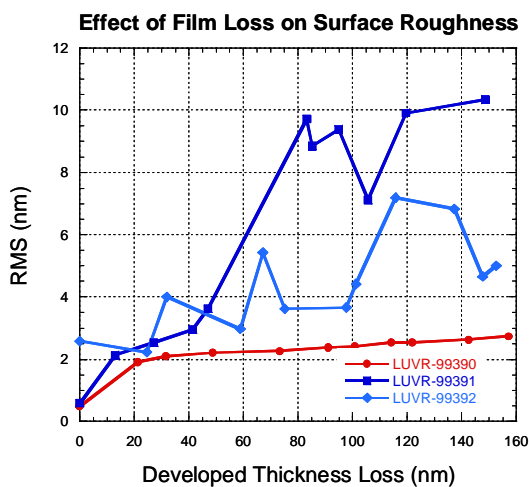
Figure 6. Depth profiling film roughness for films containing TPS-MBS based PAGs and Poly-K.

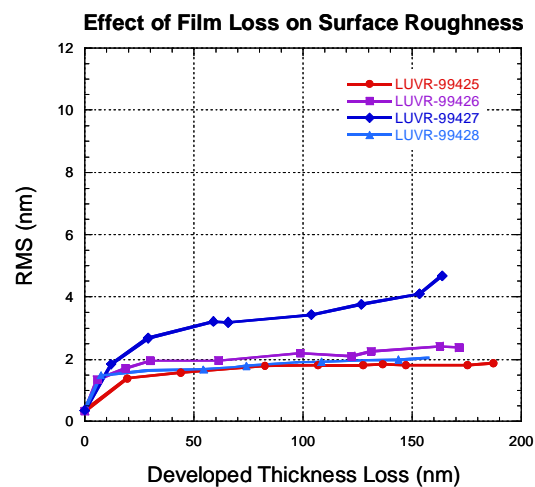**Effect of Film Loss on Surface Roughness**

Figure 7. Depth profiling film roughness for films containing PDMS-Tf based PAGs and Poly-K.

The non-dissolution inhibiting PDMS-Tf based PAG shows very different behavior as seen in Figure 7 where both the monomeric and polymeric PAGs all have relatively low IMR although the Poly-K film containing P(PDMS-Tf-37) shows significantly higher IMR than either the other copolymer or homopolymer PAG. Again it is seen from Table 2 that the IMR of the higher hydroxystyrene containing copolymer PAG has a higher IMR value.

Several conclusions can be draw from the behavior of the polymeric PAGs in Poly-K. It appears that all non-inhibiting PAGs, whether monomeric or polymeric, have low IMR with the possible exception of P(PDMS-Tf-37). This is consistent with earlier thinking that PAGs must be both inhibiting and segregating to increase the IMR significant above that of the base polymer. All monomeric PAGs, whether inhibiting or non-inhibiting, have a small but noticeable increase in film IMR with IMR values inline with those previously published.[13] Finally, some copolymer PAGs have significantly increased IMR and this value is largest with the higher hydroxystyrene incorporation. This latter fact is apparently at odds with the concept that the lower the dissolution inhibition, which would be expected and is observed with the higher hydroxystyrene incorporation, the less the IMR. It appears that these polymeric PAGs may

have a high degree of segregation unto themselves and this segregation is responsible for the higher IMR values. We have developed evidence for this higher degree of segregation and will report on it separately.

3.3. Polymeric PAG IMR with exposure and thermal deprotection

The general experimental procedure to determine the IMR present in the resist as a result of exposure and subsequent acid catalyzed deprotection was to perform our previously described simplified depth profiling procedure, in which the surface roughness of a contrast curve is measured by AFM at an interval of roughly every 5 nm of film loss.[15] This procedure was performed on six resists containing the two monomeric PAGs and 4 polymeric PAGs shown in Table 3.

Table 3. Summary of IMR for resists with various PAGs with exposure and thermal deblocking.

Resist	PAG	PAG Amount (%)	IMR (nm) at 100°C	IMR (nm) at 130°C
LUVR-99395	TPS-VBS	5.0	4.0	6.9
LUVR-99396	P(TPS-VBS-32)	16.6	3.9	6.6
LUVR-99397	P(TPS-VBS-54)	9.2	3.2	5.0
LUVR-99398	TPS-MBS	5.0	4.5	8.9
LUVR-99399	P(TPS-MBS-36)	15.0	4.2	5.4
LUVR-99400	P(TPS-MBS-70)	7.4	3.6	5.7

Figure 8 shows the RMS surface roughness of resists containing the TPS-VBS monomer and TPS-VBS containing copolymers obtained from contrast curves with a PEB of 100°C. The TPS-VBS monomer containing resist shows a periodic fluctuation of the AFM measured surface roughness as a function of developed depth into the resist film. This periodic fluctuation roughly corresponds to the exposure intensity of the standing wave but at a level that is over ten times the magnitude of the standing wave intensity change that was calculated for the resist over ARC. A second feature is that the magnitude of the roughness change for the TPS-VBS monomer containing resist increases by over a factor of two when the resist is exposed and thermally deprotected while the TPS-VBS copolymer containing resists have their IMR values slightly decrease as seen in Table 3. The RMS surface roughness of resists containing the TPS-VBS monomer and TPS-VBS containing copolymers obtained from contrast curves with a PEB of 130°C are shown in Figure 9. Here the IMR values of all three resists increase with the periodic fluctuation reduced in magnitude but sill present.

The RMS surface roughness of resists containing the TPS-MBS monomer and TPS-MBS containing copolymers obtained from contrast curves with PEB of 100°C are shown in Figure 10. Again the TPS-MBS monomer containing resist shows a periodic fluctuation of the AFM measured surface roughness as a function of developed depth into the resist film. This periodic fluctuation is not observed with either of TPS-MBS copolymer containing resists with a 100°C PEB. Figure 11 shows the RMS surface roughness of resists containing the TPS-MBS monomer and TPS-MBS containing copolymers obtained from contrast curves with a PEB of 130°C. The 130°C PEB RMS surface roughness increases for all three resists relative to that seen with 100°C PEB. The IMR values for both PEB temperatures is given in Table 3 and it can be seen that at both bake temperatures the IMR values are considerably larger that those for the same PAGs in Table 2 without exposure and subsequent acid catalyzed deprotection.

It was previously argued that if the cause of this periodic fluctuation was related to some initial inhomogeneity of the acid distribution caused by different exposure energy as a result of standing waves or different degrees of polymer deprotection as a result of small differences in the initial acid distribution then the higher PEB temperature would result in higher levels of acid diffusion that should remove these effects. In these cases the high PEB temperature again increases the magnitude of the standing wave related degree of surface roughness. The increase in the magnitude of the roughness change is consistent with thermally driven material segregation, most likely being the PAG, causing small-scale dissolution inhomogeneities.
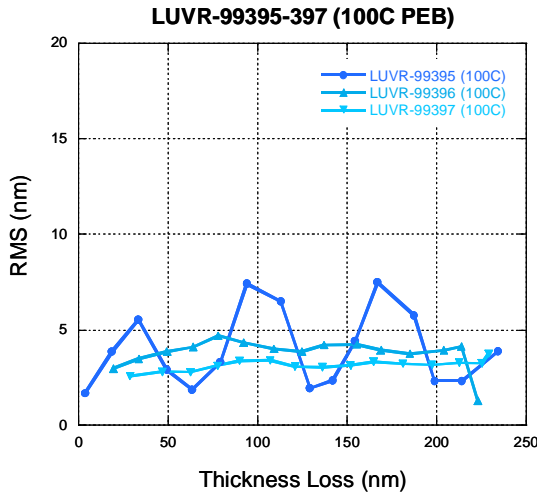
Figure 8. Depth profiling film roughness for resists containing TPS-VBS based PAGs with 100°C PEB.
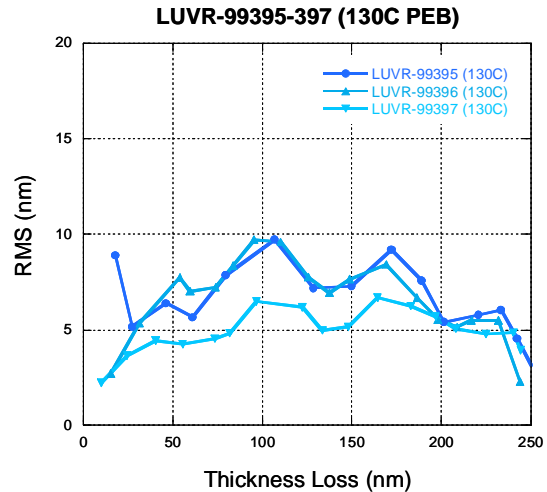

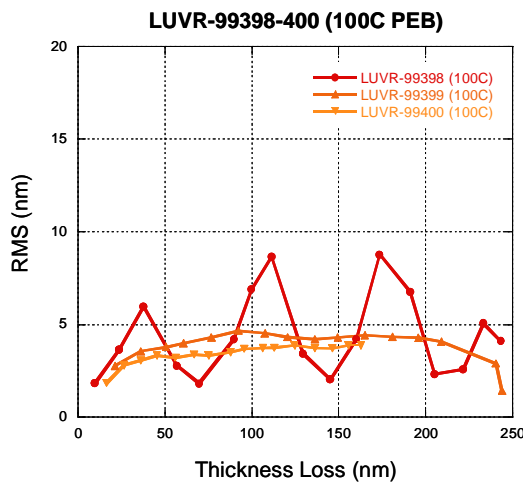**Figure 9.** Depth profiling film roughness for resists containing TPS-VBS based PAGs with 130°C PEB.

Figure 10. Depth profiling film roughness for resists containing TPS-MBS based PAGs with 100°C PEB.
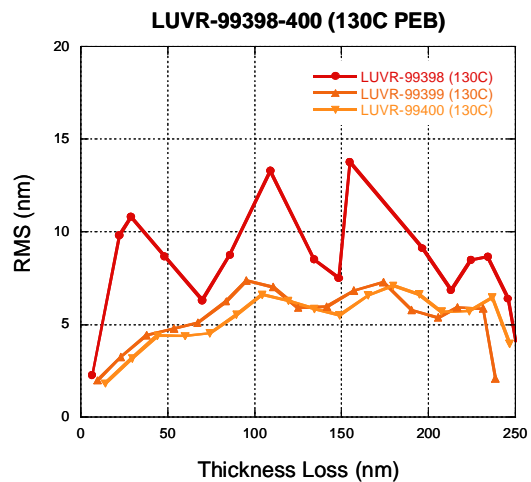

Figure 11. Depth profiling film roughness for resists containing TPS-MBS based PAGs with 130°C PEB.

The reduced level of standing wave related degree of surface roughness for the TPS-VBS and TPS-MBS copolymer PAGs is also consistent with reduced PAG diffusion resulting in lower amount of PAG segregation at the 100°C PEB temperature. Even with a 130°C PEB temperature, the standing wave related degree of surface roughness is much less for copolymer PAGs than the monomeric PAGs. This is again consistent with reduced PAG diffusion resulting in lower amount of PAG segregation for the copolymer PAGs and inconsistent with reduced PAG diffusion of polymeric PAGs yielding a higher standing wave effect relative to the monomeric PAGs.

The comparison of monomeric and polymeric PAGs at different PEB temperatures provides further evidence that PAG segregation in resists is responsible for increase RMS surface roughness and the unusual periodic fluctuation of RMS surface roughness associated with standing wave intensity. The decreases in the magnitude of the RMS roughness with the copolymer PAGs is consistent with thermally driven material segregation, most likely being the PAG, causing small-scale dissolution inhomogeneities.

4. CONCLUSIONS

We have extended our technique called resist deconstruction to probe the effect of polymeric PAGs on material roughness by studying a series of monomeric and polymeric PAGs to determine the effect of polymer-bound PAGs on IMR. In order to explore the effect of PAG phase segregation on IMR a variety of polymeric PAGs were prepared. Two series of anion-bound PAG polymers were prepared based on the previously known TPS-VBS and TPS-MBS. Copolymers of these two PAG monomers with hydroxystyrene were prepared with differing ratios of PAG and hydroxystyrene. One series of cation-bound polymers was also prepared from the previously described PDMS-Tf. The PDMS-Tf homopolymer and copolymers with differing ratios of hydroxystyrene were also prepared.

The polymeric PAG IMR both with and without exposure or thermal deprotection was determined. It was shown that without exposure or thermal deprotection, PAG copolymers with high levels of hydroxystyrene have increased levels of IMR and it appears that these polymeric PAGs may have a high decree of segregation unto themselves and this segregation is responsible for the higher IMR values. The monomeric and homopolymer PAGs have relatively low levels of IMR which is consistent with previous reports of low levels of IMR in the absence of thermal deprotection.

Resists containing polymeric PAGs showed reduced IMR relative to momomeric PAGs when exposed and thermally deprotected. The polymeric PAGs also showed reduced level of standing wave related degree of surface roughness relative to the monomeric PAGs. The increased level of IMR for both monomeric and polymeric PAGs at higher PEB temperatures provides further evidence that PAG segregation in resists is responsible for increased RMS surface roughness and the unusual periodic fluctuation of RMS surface roughness associated with standing wave intensity. The decreases in the magnitude of the RMS roughness with the copolymer PAGs is consistent with thermally driven material segregation, most likely being the PAG, causing small-scale dissolution inhomogeneities.

5. ACKNOWLEDGMENTS

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