Leaching Phenomena and their Suppression in 193 nm Immersion Lithography

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The leaching of ionic PAGs from model resist films into a static water volume is shown to follow first order kinetics. From the saturation concentration and the leaching time constant, the leaching rate at time zero is obtained which is a highly relevant parameter for evaluating lens contamination potential. The levels of leaching seen in the model resists generally exceed both static and rate-based dynamic leaching specifications. The dependence of leaching on anion structure shows that more hydrophobic anions have lower saturation concentration; however, the time constant of leaching increases with anion chain length. Thus in our model system, the initial leaching rates of nonaflate and PFOS anions are identical. Investigation of a water pre-rinse process unexpectedly showed that some PAG can still be leached from the surface although the pre-rinse times greatly exceeded the times required for saturation of the leaching phenomenon, which are expected to correspond to complete depletion of leachable PAG from the surface. A model is proposed to explain this phenomenon through re-organization of the surface as the surface energy changes during the air/water/air contact sequence of the pre-rinse process. The efficiency of developer-soluble top barrier layers in reducing leaching and their impact on lithography are described as well as the effect of PAG doping into the top layers.

Keywords: immersion lithography, photoresist, PAG leaching, kinetics, leaching rate, top protective coat, barrier coat.

1. Introduction

The implementation of 193 nm immersion lithography is proceeding with unprecedented speed. Following its introduction into the ITRS Roadmap in 2004, it has quickly emerged as the definitive successor to 193 nm dry lithography. This high rate of development has been possible due to the fact that, in sharp contrast to 157 nm lithography, many of 193 nm immersion technology's key components are essentially identical or at least very similar to their existing dry counterparts, e.g., lens materials, pellicles, or photoresists.

In the area of photoresists, in particular, the (meth)acrylate polymer platform that is dominant in 193 nm dry lithography has been shown to be well suited to adaptation to immersion lithography.¹ While immersion-specific optimization and tweaking will undoubtedly be required, it is anticipated that the existing

monomers, such as the various adamantane derivatives and lactones commonly used in 193 nm dry lithography, will also form the basis for 193 nm immersion photoresists. The stable of monomers used in this platform may possibly be augmented by fluoroalcohol-substituted derivatives, but if this development should come about, it would also be expected to occur in 193 nm dry lithography.

One unique difference between dry and immersion lithography lies in the interactions between immersion medium and photoresist. In the case of dry (or 'air immersion') lithography, concerns of lens damage from outgassing of volatile components has been a key issue; now, with water immersion, the new ability of the immersion medium to leach also non-volatile components such as ionic PAGs has further raised the level of concern. Investigations of

transmission loss due to optically induced deposition on lens elements together with studies of fluid flow and contaminant transport in the immersion medium have led to first specifications for PAG leaching; these are being discussed either in terms of a dynamic (leaching rate of <1.6 pmole/(cm² sec)) or a static (leached concentration of <0.74 pmole/cm²) leaching specification. It is therefore important to gain an accurate and quantitative understanding of the leaching phenomenon in order to determine whether existing resist formulations meet these specifications, or if they do not, to have a measurement method available for development of materials that do. In this paper, we report on kinetic investigations of PAG leaching from model systems. Based on the kinetic analysis, we propose a method for measuring the short-term leaching rates required by dynamic leaching specifications.

An alternative to the development of such 'low leaching' photoresists lies in the use of top protective layers; such layers have already been shown to reduce the leaching by more than two orders of magnitude in the best cases, and they may well make possible the use existing dry photoresists for early implementation of immersion lithography. We have previously published an initial account of our work on immersion barrier coats;X this paper will outline our recent progress in developing such materials.

2. Experimental Section

2.1 Kinetics of Leaaching

Model photoresists were formulated using a copolymer of 2-methyladamantane methacrylate (MAdMA) and β -(γ -butyrolactone (GBLMA) made by free radical polymerization in THF using AIBN initiator. The copolymer had a weight-average molecular weight (MW) of about 12,000 and a polydispersity of about 1.7. Model PAGs used were triphenylsulfonium triflate, nonaflate, and perfluorooctanesulfonate, which were obtained commercially. Model resists were formulated in PGMEA and used a PAG loading of 36 μ mole PAG per g solids. Resist films were formed by spin coating on 4" or 8" wafers and had a film thickness of about 150 nm after a softbake of 130 °C.

Leaching experiments were carried out either in the full-wafer immersion apparatus described earlier¹ or using an O-ring (4 cm inner diameter) that was directly placed on the wafer surface. For the full wafer immersion apparatus, about 45 ml of water was required for a complete fill, corresponding to a water column height of about 1.3 mm above the 8" wafer. In the case of the O-ring method, a weighed amount of water (about 4.3 – 4.9 g) was poured rapidly in to the O-ring, and taken up after the specified time interval by means of a disposable plastic pipette. No leakage was observed from the O-ring/wafer interface.

Water samples were analyzed by the LC-MS-MS technique at a commercial analytical services provider (Exygen Research, 3058 Research Drive, State College, PA16801). Results were received in units of ppb of the respective acid and were recalculated into units of picomoles of acid per centimeter squared [pmole/cm²] using the molecular weight of the acid and the weight of water introduced into the O-ring.

2.2 Topcoat Leaching and Imaging Experiments

The resist materials that we employed in this study consist of acrylate/methacrylate resins

Scheme I: Components of model photoresists used for the leaching studies.

with pendant alicyclic moieties similar in basic structures to polymers A-D in Scheme II used in early work under the auspices of the SEMATECH 193 nm immersion task force. Resists are typically

formulated in typical spin casting solvent such as PGMEA along with an amine base, such as triethylamine, and a photoacid generate such as onium salts that photochemically generating super acids, such as perfluorobutanesulfonic acid. The barrier coat material are fluorinated polymers containing base-solubilizing moieties attached to the polymer framework. These materials are dissolved in alkyl alcohols or mixtures of solvents, such as alkane with alkylesters or alkanes with alkyl alcohols, formulated such that they do not typically dissolve 193 nm resist films and thus allow the deposition of the barrier coat on top of the resist. All top coats studied are fully developer-soluble and are removed during the normal development cycle along with imaged resist.

The topcoat leaching experiments were carried out using the full wafer immersion apparatus described earlier.¹ Typically, the leaching is carried out with an 8 inch silicon wafer extracted with 50 mL of distilled water for 60 seconds. Measurement of leached perfluoroalkylsulfonates was performed by Exygen Research (3058 Research Drive State College, PA 16801, USA) using a HP1100 interfaced to a Micromass Quattro Ultimate LC/MS/MS system. A gradient elution through a Jones Chromatography Genesis C-8 50X2 mmX5 micron column was used for separation. A mobile phase gradient starting from 2 mM ammonium acetate in water to methanol was employed. The ionization mode employed was electrospray with negative polarity. Exposed samples were prepared by blanket irradiation with a HTG Lightsource 85.-3 for a sufficiently long enough time to get a dose at 248 nm of 200 mJ/cm².

Exposures at 193 nm were done with a Nikon 306D 193nm scanner employing annular Illumination; (NA=0.75 A:0.50). Coating, bake and development were done on a TEL@ ACT 12 track which was linked to the Nikon tool. Top Down SEM pictures were obtained with a KLA8100 CD-SEM: each data point taken as the average of two measurement values. CDs measured at 50% threshold with 20nm offset. Simulated Immersion experiments are performed by either using a pre-exposure or a post exposure wash for 60 seconds with distilled water.

Scheme II: Polymers used in early 193 nm immersion task force work under the auspices of the SEMATECH 193 nm, representative of the class of acrylate/methacrylate alicyclic 193 nm resist resins.

3. Kinetics of PAG Leaching

3.1 Kinetics Theory

PAG leaching has previously been shown to be a surface phenomenon by a variety of methods, e.g., NEXAFS studies of the PAG density at the resist surface^{3,4} before and after water contact, or the independence of the leached amounts on the resist film thickness.⁵ Only a small percentage of the total PAG in the film (about 3-5% for a 200 nm thick film) is actually leached. Leaching has been found to saturate fairly quickly: in the case of TPS nonaflate, radioactive labeling studies⁶ and early kinetics studies with limited time resolution¹ had shown that leached PAG levels remained constant between about 10 and 300 sec.

The simplest model that is consistent with the above observations assumes that PAG leaching is only dependent on the number of PAG molecules present at the surface. If all PAG molecules leach independently of each other and if there is no measurable back reaction (an assumption that is plausible given the large dilution of the PAG in the immersion medium), the change in the number N of PAG molecules at the surface is given by

$$\frac{dN}{dt} = -\beta N, \quad (1)$$

which leads to a simple first order kinetics law:

$$N = N_0 \cdot e^{-\beta t}, \quad (2)$$

where N_0 is the leachable PAG concentration $N_{\text{initial}} - N_{\text{final}}$. It is known from the NEXAFS experiments^{3,4} that the PAG concentration at the surface is not zero even after prolonged water contact (leading to saturation) and subsequent drying.

The time dependence of the PAG concentration C in a constant volume of water above the surface is then given by

$$C = C_{\infty} (1 - e^{-\beta t}) \quad (3)$$

For short times, the exponential can be approximated by a linear function, which yields

$$C = C_{\infty} \cdot (1 - e^{-\beta t}) \approx C_{\infty} \beta \cdot t \quad (4)$$

The leaching rate at time zero is then given by

$$\left. \frac{dC}{dt} \right|_{t=0} = C_{\infty} \beta \quad (5)$$

Figure 1 shows a schematic for the general behavior of N and C , and their relation to $C_{\infty} \beta$.

Figure 1: Schematic behavior of N and C as a function of time and their relation to $C_{\infty} \beta$.

The expected contact time for the immersion puddle with an exposure field in the currently favored showerhead configuration of immersion scanners is of the order of one second. Using only simple laboratory setups such as the full wafer immersion tool or the O-ring setup described above, there are substantial experimental difficulties associated with introducing water onto the wafer surface and retrieving it within such a short time. The determination of both the saturation concentration C_{∞} and the time constant β can, however, be easily and accurately carried out by fitting the data points for experimentally

achievable times (≥ 2 sec or so) to Eq. (3). We therefore propose this method as a general approach for determining the initial leaching rate of photoresists.

3.2. Kinetics Results

Our first attempts at measuring leaching kinetics used the full wafer immersion tool described earlier. A limitation of this tool was the time required to introduce water into it by syringe. A minimum time of 3 sec was required to fill the tool, and another 3 sec to withdraw it. Besides the undesirably long time required, this method also requires a complicated back-calculation to deconvolute the different immersion times seen for the bottom (6 sec) and the top (0 sec) of the photoresist. Figure 2 shows the time dependence of nonaflate concentration obtained with this setup for a commercial resist material with about 1.5 % w/w PAG loading. The process had already essentially saturated at the shortest experimentally available times. While the minimum immersion time could be shortened by continuing to inject water and collecting the outflow, the O-ring method was found to be a simpler, easier and faster procedure.

Analysis of the data from Fig. 2 gave a time constant β of the order of 0.4 sec^{-1} , corresponding to a half-life of leaching of about 1 to 1.5 sec. Similar results were obtained with the O-ring method for the nonaflate-based model resist described in the Exp. Section (cf. Table 1). With this method, the shortest immersion times obtained were just under 2 seconds.

The leaching behavior of the triflate and PFOS-based model resists is shown in Fig. 3, and Fig. 4 compares the leaching curves of the three model PAGs. Saturation concentrations C_{∞} and time constants β were determined by a fit to Eq. (3) and are given in Table I, together with the initial rate of leaching $C_{\infty} \beta$.

Inspection of the experimental data indicates that for the LC-MS-MS analytical method with a limit of quantitation of 50 part per trillion (ppt), the amount of noise seen in the data sets (typically at concentrations of single to double digit ppbs) is unexpectedly high. It is currently unknown whether this noise is due to limitations of the

analytical method or the sample preparation, or if it constitutes an inherent variability of the leaching phenomenon.

Figure 2: Leaching of nonaflate anion from a 200 nm thick commercial resist film using the full wafer immersion tool. Even the first experimentally accessible data point (total contact time of 6 sec) is already in the saturation region. Saturation concentration $C_{\infty} = 24.8$ ppb, estimated rate constant $\beta = 0.4 \text{ sec}^{-1}$.

Figure 3: Leaching of triflate and PFOS anion from a 150 nm thick model resist film formulated as described in the Exp. Section. Data were generated using the O-ring method and analyzed via non-linear least squares fit to Eq. (3). Fit parameters are given in Table I.

The comparison of the anion dependence of leaching (Fig. 4 and Table I) shows that when

expressed in molar units, nonaflate and triflate have similar saturation concentrations C_{∞} ,

Table I: Saturation leaching concentrations C_{∞} , time constants and initial leaching rates for model PAGs.

Anion	C_{∞} [pmole/cm ²]	β [1/sec]	τ [sec]	$(dC/dt)_{t=0}$ [pmole/(cm ² sec)]
Triflate	6.7	0.23	3.0	1.56
Nonaflate	6.3	0.43	1.6	2.71
PFOS	4.1	0.68	1.0	2.75

Figure 4: Comparison of leaching curves in molar units for model resists containing TPS triflate, nonaflate, and PFOS.

while that of the PFOS salt is noticeably lower (note that in terms of weight (ppb) units, the results is quite different due to the different molecular weights of the acids as given in Scheme I). At the same time, the time constants β of leaching increase in the sequence $\text{PFOS} > \text{Nf} > \text{Tf}$. This has the effect of PFOS and nonaflate having the same initial leaching rate $C_{\infty} \beta$, whereas that of triflate is smaller by almost a factor of two. The consequences of this behavior for immersion PAG design are discussed in Section 5 below.

It has been suggested that since the leaching phenomenon saturates, it should be possible to eliminate all leaching by a water pre-soak process. We allowed a stream of water to flow over wafers coated with the resist of Fig. 2 for periods of 30 or 60 sec; the wafers were then dried with a compressed nitrogen jet and analyzed with the full wafer immersion setup. The results of the

experiment are shown in Fig. 5. Unexpectedly, it was found that not only were there measurable nonaflate concentrations detected, but they also again followed first order kinetics. However, the saturation concentration for the pre-rinsed wafers lies at only about 12% of that seen for the non-rinsed wafers, and the time constant has decreased by a factor of about 2. No difference was observed in either of the kinetic parameters for the 30 and 60 sec pre-rinse times. A model for this unexpected behavior is discussed in Section 5 below.

Figure 5: Kinetics of leaching for wafers pre-rinsed with water for 30 and 60 sec. Both data sets are well fitted by a single set of parameters $C_{\infty} = 3.0$ ppb and $\beta = 0.18 \text{ sec}^{-1}$.

3.3 Discussion

The data collected for all model systems are consistent with first order kinetics for ionic PAG leaching. Analysis of the data using Eq. (3) gives reasonable fits within the (not inconsiderable) noise level of the experiment. Both the saturation leaching concentrations C_{∞} and the initial leaching rates $C_{\infty}\beta$ are obtained from the fit. We therefore suggest the use of this method for the determination of both the static and dynamic leaching parameters.

Inspection of Table I shows that the experimentally determined saturation leaching concentrations C_{∞} of the model resists exceed one exposure tool vendor's specification of 0.74 pmole/cm^2 by factors of six to twelve, and the initial leaching rates $C_{\infty}\beta$ are at or above the dynamic leaching spec of $1.6 \text{ pmole/(cm}^2 \text{ sec)}$ set by a second tool vendor. Only TPS triflate comes

close to meeting the dynamic specification, although it is by far more soluble than TPS nonaflate or PFOS. Presumably, this result is due to the triflate's lower tendency to accumulate at the surface which appears to be correlated with a slower rate constant β . However, the use of triflate in high resolution photoresists is severely limited by the high diffusion rate of triflic acid. It is therefore clear that resist formulations and components will need to be optimized in order to enable the use of photoresists without top protective coatings.

One possible strategy is the modification of the ionic PAGs for higher hydrophobicity. Such a modification can occur either in the anion or in the cation component of the ionic PAG. As exemplified by TPS PFOS, larger, more hydrophobic PAGs can have lower saturation concentrations C_{∞} (Fig. 3 and Table I). However, this PAG also shows a higher leaching time constant β , possibly as a result of a stronger tendency of the PFOS amphiphile to aggregate at the surface. As a result of this, the product $C_{\infty}\beta$ is the same for nonaflate and PFOS, and there is no advantage in the initial leaching rate. New types of anions will be required that combine low diffusivity with lower surface affinity. Further experiments with modification of the cation are planned, but it is already clear that at least for the dynamic leaching specification, it will not be sufficient to show a decrease in C_{∞} alone but that the initial leaching rates $C_{\infty}\beta$ will have to be determined in a kinetic experiment. A second approach, not currently investigated in this study, is to dispense with ionic PAGs entirely and to use non-ionic PAGs that may have intrinsically higher hydrophobicity.

The exponential rate law suggests that the PAG has a binding energy that must be overcome for leaching (=desorption) to occur. Leaching rates should then follow an Arrhenius-type law:

$$\beta = Ae^{-\frac{E_a}{RT}} \quad (6)$$

However, it is already obvious from the short time constants observed that the activation energy of leaching is quite low. Using a typical collision factor of $A = 10^{13}$ and a time constant β of the

order of 1 sec^{-1} , one obtains for immersion at $\sim 300\text{K}$ temperature

$$E_a = -RT \ln \frac{\beta}{A} \approx 32RT = 9-10 \left[\frac{\text{kcal}}{\text{mole}} \right] \quad (7)$$

With an activation energy of this size, either a large temperature range or high precision in the rate constants will be required to experimentally determine either A and E_a or $\Delta H^\ddagger$ and $\Delta S^\ddagger$ by the usual temperature-dependent measurements. With a maximal practical range of immersion temperatures of about 60°K , one would require a precision of at least 4% for the determination of the rate constants. However, the present noise level in the data is closer to 10%, and an experimental determination of the activation parameters will have to await the development of a more precise method.

An unexpected result was observed in the pre-rinse experiments, in which a wafer was subjected to continuous water flow for 30 or 60 seconds. Subsequent re-immersion showed that there was renewed leaching at about 12% of the original rate, a result that is *prima facie* inconsistent with the observed saturation behavior: saturation is assumed to occur only if all leachable PAG has been removed from the surface. However, the fact that no difference was observed between the 30 and 60 second immersion data sets is consistent with saturation. The apparent contradiction can be resolved if one assumes that the surface is changed after immersion as a result of the drying process. The existing data are consistent with the following model for the leaching and re-leaching phenomena:

- During spin coating and bake, the PAG is enriched at the low energy air/resist interface. The degree of enrichment is determined by the nature of the PAG. More hydrophobic materials have a higher tendency to migrate to the surface, in particular if one of the components can orient itself to present long hydrocarbon or fluorocarbon chains to the air interface.

- During immersion, the air is replaced by water and the nature of the interface changes to a high energy interface. PAG is dissolved away from the surface following first order kinetics; all

leachable PAG has left after a few seconds, and the surface is PAG depleted. At the same time, water begins to diffuse into the resist following standard Fickian diffusion. It is possible that some PAG migrates away from the high energy interface and is entrained by the water migrating into the film. From the measured water diffusion constants,³ the system is far from reaching equilibrium within typical immersion times.

- After the water is removed from the surface, the resist film begins to dry out. The resist surface again contacts air and now again is a low energy interface that favors hydrophobic/fluorinated components. The motion of water diffusing out of the film entrains some PAG and moves it back to the surface. PAG re-populates the surface and regenerates a layer of leachable PAG, albeit at much lower levels than originally.

Although the pre-rinse process does reduce leaching rates to levels commensurate with vendors' specifications, there are indications of a decrease in exposure latitude and process window associated with it.⁷ Also, increased defectivity due to a pre-rinse is a matter of concern, and further work is required for a final verdict on the viability of this process.

4. Topcoat Leaching Experiments

4.1.1 Studies on AZ[®]1120P Resist

The commercial AZ[®]1120P resist was used as a benchmark for many of our leaching studies. Figure 6 compares the amount of perfluoroalkylsulfonate leaching obtained from the full wafer leaching experiments for non-exposed and exposed AZ[®]1120P resist films. The exposed films had essentially all of the PAG converted to photoacid at a dose of 200 mJ/cm^2 . Consequently, the "exposed experiment" gives a measure of photoacid leaching while the unexposed give the value for the PAG itself. At the lambda quarter plate thickness of 32 nm, both AZ[®]EXP ITC1100 or AZ[®]EXP ITC1400 barrier coats substantially decrease the amount of leaching from AZ[®]1120P resist. From the limited set of data points, it appears that AZ[®] ITC 1400 may be somewhat better at preventing leaching of PAG while AZ[®] ITC1100 is better at preventing leaching of photoacid (Figure 6). However, in

both instances there appears to always be some residual amount of PAG extracted through the thin barrier coat. The amount of PAG extracted can, however, be further reduced by using barrier coats thicker than a $\lambda/4$ plate. Several groups have reported on PAG concentration gradients in top coat films⁸ by using a mechanical means of cross-sectioning the thin films at a highly oblique angle, followed by direct mass-spectroscopic observation of the PAG concentration as a function of position. In these studies, substantial differences in the ability of the top coats to immobilize and contain the PAG over a short distance have been observed. Among the factors contributing to these differences we have identified the extent of PAG dissolution by the top coat casting solvent and the ability of the top coat material to retain the PAG once it has left the resist film.

By doping a barrier coat spinning solution with differing amount of PAG we were able to estimate how well the topcoats retain PAG even when it is already present in the spinning solution. Figure 7 shows a study done with AZ[®] ITC 1100 doped with differing amounts of PAG. It is seen that deliberately doping with PAG does not really dramatically increase the amount of leaching observed. Indeed, the amount of leaching appears to not vary very much, even when increase the loading of PAG by a factor of ~ 5 . There are two conclusions to be drawn from this experiment: 1. the polymer used for this particular top coat shows a strong interaction with the PAG,⁹ and 2. it is possible to consider doping of barrier coats with PAG as an approach to modify the behavior of this material without undue increase in the amount of PAG leaching. Depending on resist and barrier coat type, in some cases one can utilize PAG doping of top coats to lithographic advantage, e.g., for the modulation of T-topping tendencies.

4.2 Simulated Immersion Studies with AZ[®]1120P Resist

Simulated immersion studies were also done of the different barrier coats using, as in the dry lithography studies, AZ[®] 1120p as a reference material. This evaluation was done for barrier coats AZ[®] EXP ITC 1400, AZ[®] EXP ITC 1100 and AZ[®] EXP ITC 1300.

Figure 6: Full wafer extraction of AZ[®] EXP1120P films (200 nm) without a barrier coat and with two different types of immersion topcoats, AZ[®] EXP ITC1100 and AZ[®]EXP ITC1400. Extraction duration 60 seconds. Exposed films were exposed to ~ 200 mJ/cm² using a Hg Arc Lamp.

Figure 7: Full wafer extraction of AZ[®] EXP1120P films (200 nm) without and with a the AZ[®] EXP ITC 1100 barrier coat doped with increasing amounts of PAG. Other conditions as in Figure 6.

In the simulated immersion work the wafers were exposed using standard 193 nm dry lithography, but the wafers were either washed with water prior to exposure or right after exposure. This was done to gauge the combined effect of depletion of PAG or photo acid by leaching with water combined with any possible impact brought about by application of the topcoat itself. One possible impact of barrier coat application, as was previously discussed, is removal of PAG from the resist by the casting solvents of the barrier coat.

Generally, it was observed that the use of a barrier coat, coupled with pre or post-exposure washing with water, does significantly affect the

performance of AZ® AX1120P resist. Figure 8 illustrates this type of study with the barrier coat AZ® ITC 1400. As can be seen by inspection of the Figure, the AZ®EXP ITC 1400 barrier coat does not cause any deterioration in resist performance during simulated immersion, regardless of whether it is used as a dry top coat, or with pre-exposure or post exposure water rinses. This is not automatically always the case for all top coats: a similar situation obtains as in dry lithography with aqueous-based top antireflective coatings, where the photoresist chemistry and the acidity of the materials must be matched to each other.

5. Conclusion

We have shown that the leaching of ionic PAGs from model resist films into a static water volume follows first order kinetics. A fit of the leaching data to the first order reaction equation

yields both the saturation concentration and the leaching time constant. Their product is the leaching rate at time zero, which is a highly relevant parameter for purposes of evaluating the lens contamination potential because of the dynamic water dispense and short water contact time of typical full field immersion tools. We suggest the use of this fitting method for the determination of both the static and dynamic leaching parameters.

The levels of leaching seen in the model resists greatly exceed one vendor's concentration-based static leaching specification and are at or above another vendor's rate-based dynamic leaching specification. It appears that resist formulations and components will need to be optimized in order to enable the use of photoresists without top protective coatings. The dependence of leaching on anion structure shows that more hydrophobic anions can lead to a

Figure 8: AZ®AX1120P (200 nm) coated with AZ® ITC 1400 (32 nm) on AZ® ArF-1C5D bottom coat (36.9 nm @ 2763rpm). SB 130°C/60s, PEB 130°C/60s, DEV AZ®300MIF/60 s. Comparison of no rinse, and 1 min pre or post-exposure rinse with distilled water (60 seconds).

decrease in saturation concentration; however, simultaneously the time constant of leaching increases with increasing anion chain length. This leads to the effect that in our model system, the initial leaching rates of nonaflate and PFOS anions are identical. Further work is needed to determine the impact of cation modifications and to investigate low diffusion anions with lower surface accumulation tendency.

Investigation of a water pre-rinse process unexpectedly showed that some PAG can still be leached from the surface although the pre-rinse times greatly exceeded the times required for saturation of the leaching phenomenon, which are expected to correspond to complete depletion of leachable PAG from the surface. A model is proposed to explain this phenomenon through reorganization of the surface as the surface energy changes during the air/water/air contact sequence of the pre-rinse process.

The present kinetics study has focused on the leaching of intact PAG and has excluded the leaching of photoproducts following exposure, i.e., free photoacid and the various cation photoproducts. It is known from earlier studies that leaching of photoacid following exposure can lead to higher saturation concentrations of the anion than observed in the unexposed film,^{1,2,3} while radioactive labeling of the TPS cation has indicated that the saturation concentrations of intact TPS and of its photoproducts are comparable.⁶ However, saturation concentrations alone are not sufficient to determine the initial leaching rates, and further work is planned to extend this study to exposed model resist films.

The barrier coats have demonstrated a good capability to retain PAG, and extra PAG added to the barrier coat formulation does not greatly increase the amount of PAG leached from the resist surface. Dry and simulated immersion studies show that properly optimized barrier coats have no effect on performance of a commercial 193 nm dry photoresist resist, although T-topping or film loss can be seen in simulated post exposure immersions if there is a mismatch between the materials. It appears that the effect of barrier coat on imaging is a complex interweaving of the effect of PAG and photoacid leaching by water, the effect of application of the barrier coat,

and the nature of barrier coat itself on the imaging capability of the resist. Due to the relatively high level of leaching seen in current 193 nm photoresists, success in the design of barrier coats will be crucial for early implementation of 193 nm immersion lithography.

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