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ABSTRACT

The addition of a surface conditioning agent to the de-ionized water rinse used to quench the photoresist development process is an attractive methodology to control resist line edge roughness (LER) and defectivity levels during lithographic patterning. The use of additive-containing rinses involves the interfacial adsorption of the surface-active material (e.g. ionic surfactants, neutral polymers, polyelectrolytes) and/or its penetration into the patterned resist structure, which can be held responsible for polymer chain relaxation and reorganization within the resist matrix, resulting in reduced LER. The non-specific adsorption process can also lead to the creation of repulsive (electrostatic or steric) forces between additive-coated surfaces, thus allowing for particulate stabilization in the rinse liquid and the minimization of printable defects. In this study, LER improvement (8 % to 16 %) induced by an organic salt and defectivity reduction (*ca.* ×100) created by a polyelectrolyte contained in the rinse liquid are demonstrated in advamced 193 nm resist systems. Also, additive adsorption to a 193 nm resist surface is monitored using a quartz crystal microbalance (QCM), while the repulsive force created between additive-coated surfaces is detected using atomic force microscopy (AFM) and the presence of residual additive is quantified using total x-ray reflection fluorescence (TXRF), near edge x-ray absorption fine structure (NEXAFS) spectroscopy and contact angle measurements. The experimental data provided supports the proposed mechanisms leading to LER and defectivity improvement.

Subject terms: line edge roughness; LER; resist defectivity; surface conditioning; surfactants; rinse additives; adsorption.

1. INTRODUCTION

The continued shrinking of dimensions that is required in order to keep up with the scaling demands in modern microelectronic applications has been largely based on the success of the lithographic processes to respond to the challenges in fabrication. However, the continuous trend for smaller feature size dimensions renders this task more and more demanding. With the nearing inception of sub-50 nm lithographic nodes in manufacturing lines, imaging capabilities are challenged by stringent requirements for imaging materials that can simultaneously provide high spatial resolution, sensitivity, etch selectivity and aspect ratios, together with low absorbance, line edge roughness (LER) and defectivity, among other parameters. Given the delicate balance existing between some of the aforementioned factors, alternative processing methodologies that can address such variables individually are desirable.

In this work, we explore the use of additive-containing rinse solutions as a post-processing technique to independently achieve LER improvement and defectivity reduction on patterned photoresist structures. Incorporating additives to the final deionized (DI) water rinse used to quench the development step has been practiced in the past. The extent of LER reduction afforded by surface-conditioning rinses has been described recently[1,2], while the use of rinse additives to reduce satellite spot defects in patterned structures has previously been reported[3,4]. An additional lithographic application of additive-containing rinses is the prevention of pattern collapse, which has been extensively studied[5] and has been adopted by advanced semiconductor manufacturing facilities worldwide. However, a unified methodology that could address the consecutive improvement of LER, defectivity and pattern collapse through the use of

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rinse additives and a dedicated hardware system has not been reported yet, and potential incompatibility issues between the different rinse chemistries remain unexplored.

Here, metrology data showing improvement in LER and defectivity for a variety of 193 nm resist systems treated with a wide range of rinse additives are presented. Simultaneously, the underlying mechanisms that lead to improvement in the parameters under discussion are explored based on fundamental studies that unveil the basic role of such additives and its ultimate advantages and limitations during resist processing.

2. EXPERIMENTAL

2.1 Materials

All photoimageable materials were positive-tone resists. Single layer 193 nm resists were based on adamantane acrylate–co-lactone acrylate resins[6] used in conjunction with an appropriate organic antireflective coating. A 193 nm bilayer resist was a silane containing norbornene-maleic anhydride terpolymer[7]. For defectivity studies, only bare silicon wafers (200 mm) were used in order to eliminate potential background defectivity due to unnecessary stacking of multiple underlayers. Water-soluble additives included ionic surfactants, organic salts, non-ionic polymers and polyelectrolytes.

2.2 Processing

All bare Si wafers were inspected with a SURFSCAN[†] inspection tool (KLA-Tencor) prior to use to ensure that all initial surfaces bear uniform and low defect levels

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[†] Certain commercial equipment and materials are identified in this paper in order to specify adequately the experimental procedure. In no case does such identification imply recommendations by the National Institute of Standards nor does it imply that the material or equipment is necessarily the best available for this purpose.

(less than 20 counts). Resist imaging at 193 nm was generated using a 0.75 NA scanner (ASML) with annular illumination. Resist processing (coat, bake, develop, rinse) was carried out on an ACT-8 track (Tokyo Electron Kyushu, Ltd.). A Linear Drive (LD) nozzle was used to dispense the developer solution, which was performed using a single static puddle. Development was performed using surfactant-containing 0.26 N TMAH (track-applied), while in selected cases hand-dispensed additive-free aqueous 0.26 N TMAH (Shipley) was used. Rinse additive solutions were filtered through 0.1 μm pore size filters (Millipore). The selected aqueous additive solutions were hand-applied over the developer bowl during the rinse step (dispensed volume: 200 mL; contact time: 10 s; spin speed: 50 rpm (5.2 rad/s)), followed by a standard track-applied DI water rinse step (dispensed volume: 83 mL, contact time: 10 s, spin speed: 600 rpm (62.7 rad/s)). Duplicate wafers were generated for each particular additive-containing rinse tested.

2.3 Metrology

Linewidth roughness (LWR) is defined as 3σ of the measured linewidth values, where σ is the standard deviation, whereas line edge roughness (LER) can be derived as LWR/$\sqrt{2}$, provided that both edges of the line are uncorrelated. Since the objective of this work is to look for relative roughness variations with respect to control samples it is irrelevant which one of the two metrics is selected. For the purposes of this work, a parameter named SigmaB (AMAT) has been used as the LER metric. This parameter is the average of the 3σ LER values for each side of a photoresist line. LER values are reported as the average of 36 measurements in identical die for each wafer. Feature sizes consisted of (70-80) nm lines (either isolated or at relaxed pitch). Individual LER

measurements were obtained from 64 linewidth determinations using a NanoSEM-3D SEM (Applied Materials). The same instrument was used for defect inspection, in conjunction with a COMPASS optical inspection system (Applied Materials) that counted the total defect counts on all patterned wafers.

2.4 Instrumentation for fundamental studies

The additive adsorption kinetics to specific resist surfaces was measured using a quartz crystal microbalance (QCM) instrument utilizing 5 MHz quartz crystals (Maxtec, Inc.) with a sensitivity of 0.055 Hz ng^{-1} cm^{-2} and a PM6654C timer/counter (Keithley). The QCM wand holding the resist-coated quartz crystal was immersed in a temperature-controlled DI water bath, where adsorption processes were monitored. An alternative method used a M-2000 spectroscopic ellipsometer (J.A.Woollam) in conjunction with a liquid cell. Spectroscopic Ellipsometry (SE) data were acquired over a wavelength range of (450-1000) nm, at an incident angle of 70°. In this case, the interfacial thickness increase due to additive adsorption was monitored for photoresist films that were processed identically. A comparison between the two methods is given elsewhere.[8]

Total reflection x-ray fluorescence (TXRF) was used for chemical analysis of treated surfaces, utilizing a TXRF300 (Rigaku Corporation) instrument provided with a rotating anode X-ray generator and a Si (Li) solid-state detector.

Near edge x-ray absorption fine structure (NEXAFS) spectroscopy measurements were conducted at the U7A beam line of the National Synchrotron Light Source at Brookhaven National Laboratory. The spectra were collected with the incident beam at the magic angle (54.7°) relative to the sample to remove any polarization dependence.

The relative uncertainty in the NEXAFS intensity is less than 5 % and was determined by multiple scans on a sample. Detailed experimental conditions have been described elsewhere.[9]

Atomic force microscopy (DI 3100 AFM, Digital Instruments) was used in air with standard silicon tips (tapping mode) to image the topography of dry unpatterned resist surfaces. Captured topographic profiles (5 μm × 5 μm) were subject to a second-order plane fit before calculating the root-mean square (rms) roughness with standard Digital Instruments software. AFM measurements in liquid environment[10] (force mode) were accomplished using a liquid cell attachment and silicon nitride tips (nominal spring constant 0.12 Nm^{-1}) that were pre-cleaned by exposure to O_2 plasma. The captured force curves were processed using SPIP software (Image Metrology).

3. RESULTS

3.1 LER Reduction

General screening of a selected battery of additive-containing rinses tested on model 193 nm single layer resist systems was conducted in a previous study[4] as a way to identify the best candidate for LER reduction. Among all additives tested, it was noticeable that an organic salt was able to induce the largest statistically relevant reduction in LER, compared to all other rinses tested. Given that encouraging initial results were obtained for this salt, we set out to determine if this particular additive was able to induce a LER improvement in multiple 193 nm resist platforms. A rinse additive that could improve LER for a variety of resist systems would enable an easy implementation of the rinse solution across different lithographic nodes and resist levels.

Table 1 shows the results for the evaluation of five resist systems treated with an organic salt-based rinse (1 % by mass). A generalized LER reduction was detected for resists #1 to #4 (8 % to 16 %), whereas for resist #5 a slight increase in LER was observed (-6.5 %). Interestingly, a larger relative LER reduction was achieved by the use of the rinse additive when the resist structures were initially rougher after conventional processing (DI water rinsed samples). This result might suggest that the effectiveness of the rinse additive at reducing LER is related to the absolute amplitude of the pattern edge roughness. Based on the data presented below, it is possible to speculate that this organic salt-based aqueous rinse could be used on a wide variety of resist chemistries, however it is not discarded that particular resist systems will require specific additives in order to achieve optimum LER reduction.

Table 1. LER statistics for single layer 193 nm resist systems treated with an organic salt-containing rinse (1 % by mass).

Resist	LER (3σ, nm)		LER improvement (%)
	DI water rinse	rinse additive	
#1	$6.1 \pm 0.2_5$	5.6 ± 0.2	8.2
#2	6.7 ± 0.2	6.1 ± 0.2	9.0
#3	6.7 ± 0.2	5.9 ± 0.1	11.9
#4	8.3 ± 0.5	7.0 ± 0.2	15.7
#5	$9.2 \pm 0.2_5$	$9.8 \pm 0.2_5$	(- 6.5)

One of the most important parameters to consider when optimizing an additive-containing rinse for LER reduction is the optimum additive concentration range, since an increased additive concentration may unnecessary overload and eventually saturate the rinse performance. The organic salt additive was used to evaluate the dependence of the extent of LER reduction on additive concentration for resist #1. A broad concentration

range (0.01 % to 10 % by mass) was selected to investigate potential photoresist plasticization and flow in the presence of high additive concentrations. Table 2 shows the variation in LER and CD with increasing amounts of additive. A monotonic decrease in LER is verified up to 1 % by mass, while a higher concentration (10 % by mass) does not provide further LER decrease. One possible explanation for the existence of a limiting concentration beyond which no further decrease in LER is observed is based on the fact that many of the additives self-aggregate to form micelles in aqueous solutions due to their surfactant-like nature, which poses a limit to the concentration of non-associated additive.

Table 2. Effect of organic salt concentration on the extent of LER reduction and CD variation for resist #1.

Additive (% mass)	LER (3σ, nm)	CD (nm)
0	6.0	78.3
0.01	5.8	82.1
0.10	5.9	81.2
1.0	5.6	77.0
10	5.6	75.0

The dependence of CD variations on additive concentration was also monitored in the above experiment. CD values increase slightly (+2.5 %) at relatively low concentrations (0.01 % to 0.1 % by mass), however values closer to the control wafer were observed at higher concentration (1 % to 10 % by mass). It is possible that the variations observed in CD are due to the fact that the hand-apply process used for this study is a relatively inconsistent application method and as a result less uniform linewidth values are obtained across the wafer.

The use of surface-conditioning treatments like the one presented in this work should be checked for conspicuous pattern flow mediated by swelling and plasticization effects that can result from the potential permeation of the additive into the resist material. Such an effect might not be easily detectable through CD measurements, since often times it is evidenced by resist footing or scumming. Figure 1 shows cross-sectional profiles for patterns of resist #1 treated with the organic salt additive. The pattern profile integrity is preserved at a high additive concentration (10 % by mass) and no pattern flow is verified. In this respect, acrylate-based single layer 193 nm resists were found to be fairly insensitive to the chemical nature of the rinse additive for a wide variety of systems investigated. Additive-containing rinses used for defectivity control (Section 3.2) were found to be equally compatible.
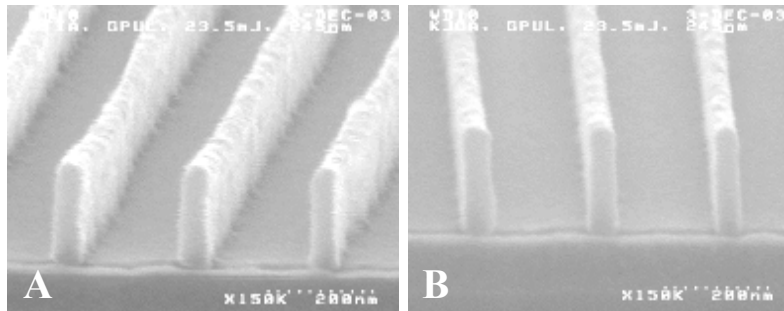
Figure 1. Effect of a rinse additive on cross sectional pattern profiles of resist #1. A) DI water rinse; B) Organic salt based- rinse (10 % by mass).

At this point, it is relevant to compare the effect of incorporating additives to a DI water rinse to the impact created by using the same additive in the developer solution, in order to achieve reduced LER values. Standard developers (TMAH aqueous solutions) usually contain additives in low concentrations. The historical need to add surface-active

chemicals to developer solutions is based on the hydrophobic nature of resist surfaces, since poor wetting of the resist by the developer can impact CD uniformity across the wafer, resulting in reduction of CD control.[11] The addition of surfactants to developer solutions improves surface wettability and leads to a more uniform development process.

In order to compare the performance of additive-containing developers to that of additive-containing rinses, rinse and developer solutions were prepared using an organic salt additive chemically similar to the one investigated previously. This additive was blended with surfactant-free 0.26 N TMAH to obtain 1 % by mass solutions. Hand-development was carried out by immersion in a developer pool followed by thorough rinsing of the processed wafer. Additive-containing developer was rinsed with pure DI water, while additive-free developer was rinsed with additive-containing rinse. A control wafer consisted of additive-free developer rinsed with pure DI water. Results for CD and LER variations for each situation are shown in Table 3. Comparable LER reduction (8 %) was detected when this additive was included in the developer or the rinse formulations, probably implying that the mechanism leading to reduced LER is identical in both cases. However, when the additive containing rinse was used, the CD was closer to the control wafer. This may be due to the faster dissolution rates observed with the addition of surfactants to developer solutions, reported previously[11].

Table 3. Effect of organic salt -containing developer vs. organic salt-containing rinse on CD and LER for resist #1.

Resist Processing	LER (3σ, nm)	CD (nm)
Additive-free development (control)	$6.5 \pm 0.1_5$	79.3 ± 0.3
Additive-containing TMAH	6.0 ± 0.2	74.8 ± 0.2
Additive-containing rinse	6.0 ± 0.1	77.2 ± 0.3

3.2 Defectivity Control

Extensive additive-containing rinse screening was performed in a previous study[4] concluding that a polyelectrolyte additive was highly effective at reducing defect counts for 248 nm and 193 nm resists. However, it was not possible to rule out that for optimum rinse performance resist-specific rinse additives might be required. A summary of the performance of a polyelectrolyte rinse for different resist platforms is shown in Table 4. The ability of an additive-containing rinse to reduce the defectivity occurrence by approximately two orders of magnitude is demonstrated.

Table 4. Measured defectivity count for a variety of 248 nm and 193 nm resists treated with a polyelectrolyte-containing rinse. Values given represent total defect counts per wafer. Duplicate samples were averaged in all cases.

Resist	Defect Count	
	DI water rinse	rinse additive
#1	4517	65
#2	10644	78
#3	27846	220
#4	5085	39

In order to clearly exemplify the effectiveness of such rinses at reducing the extent of defectivity as a function of additive concentration, a non-ionic polymeric additive was selected based on its ability to inhibit defect formation on a 193 nm bilayer system[4]. Results for the rinse additive performance are given in Table 5. A consistent decrease on the total defect count with increased additive concentration is observed. For the highest concentration tested a *ca.* × 100-reduction factor in the total number of defects with respect to the control wafer was achieved. Considering that the hand-apply process used for this study is not only a relatively inconsistent application method but

also a non-optimized one, it is reasonable to believe that an optimized, track-applied rinse additive process would bring the defect count to even lower values.

Table 5. Effect of additive concentration on the extent of defect reduction for a 193 nm bilayer resist. Values given represent total defect counts per wafer. Duplicate samples were run in all cases. Additive: non-ionic polymeric surfactant.

Additive (% mass)	Defect Count
0 (control)	4058
0.01	1627
0.1	546
1.0	44

The beneficial effect induced by an additive-containing rinse can be compared to other possible processing variables available to mitigate the extent of resist defectivity. From a track-processing perspective, few alternatives are available due to the highly automated nature of the development process. Table 6 shows a comparison of an extended DI water rinse (triple puddle) to the effect caused by different rinse times when using an anionic surfactant as rinse additive.

Table 6. Effect of various development recipes on the extent of relative defect reduction for a 193 nm bilayer resist. Duplicate samples were averaged in all cases. Rinse additive: anionic surfactant, 0.05 % wt.

Resist Processing	Relative defect count
Single DI water puddle (10 s)	1.00
Triple DI water puddle	0.38
Rinse additive - 1.5 s	0.12
Rinse additive - 10 s	0.07

It is clear that the defects attached to the wafer surface are not removed by the mechanical work introduced during repeated DI water rinses as efficiently as in the case where an additive-containing rinse solution is applied, even for a minimum period of time.

3.3 Fundamental studies

The purpose of the following studies aim at understanding the fundamental mechanisms that lead to LER and defectivity reduction achieved by the additive-containing rinses employed. Resist-rinse interfacial interactions ranging from additive adsorption to the resist surface to enhanced polymer mobility induced by additive penetration can play a critical role that determines the intrinsic performance of each particular chemistry tested.

3.3.1 Roughness reduction on developed resist surfaces

The LER reduction induced by the rinse additives on 193 nm resist systems can be compared to the effect of those additives on the surface roughness of lightly exposed blanket resist films. Variable-dose open-frame exposures followed by standard development were used to generate varying degrees of initial roughness on resist #1. Those surfaces were subsequently treated with the organic salt-containing rinse (1% by mass) for different times and finally rinsed with DI water and dried. The resulting surface morphologies were captured using AFM (tapping mode) and the corresponding 2D images were used to generate rms roughness values (Figure 2).
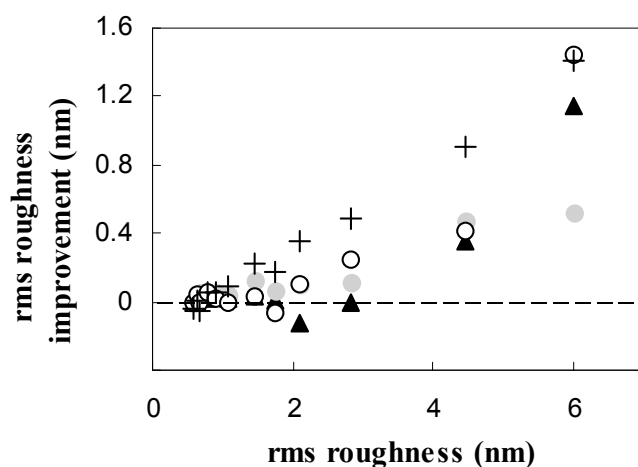
Figure 2. Roughness reduction on partially exposed resist surfaces treated with an organic salt-containing rinse (1 % by mass) for variable times, rinsed with DI water and dried. (▲) 10 s; (●) 1 min; (○) 5 min, (+) 20 min. Dose range 2 mJ/cm^2 to 5 mJ/cm^2.

It is noticeable that long contact times (20 min) induced the largest surface roughness reduction. However, even contact times amenable to manufacturing processes (*ca.* 1 min or less) were also able to produce smoother surfaces. A more pronounced decrease in surface roughness was noticeable for those surfaces that were initially rougher (exposed at higher doses), in agreement with the trends observed for patterned structures in Section 3.1 (Table 1). In addition, the relative reduction on surface roughness observed for this resist after contact for 1 min (*ca.* 8 %) is comparable to the extent of LER reduction reported in Section 3.1 for patterned features of this same resist, treated for the same contact time. These results indicate that the resist protrusions generated through the development of a partially exposed blanket film could be used as model structures, in order to analyze the effect of additive-containing rinses on the edge roughness of patterned films.

3.3.2 Additive adsorption to resist surfaces

Additive adsorption to resist surfaces was probed using a QCM and SE. These techniques measure the adsorbed layer mass and the adsorbed layer thickness attached to the resist surface, respectively. In the case of the QCM measurements water uptake was initially monitored, taking into account the frequency variations due to the density and viscosity changes of the surrounding environment upon immersion. After reaching equilibrium, an additive solution was injected with constant agitation, and the frequency changes were monitored as a function of time. As the additive adsorbs a decrease in frequency is observed. This frequency shift is proportional to the mass of the growing interfacial layer. Direct conversion of frequency shift values to adsorbed additive mass requires that the adsorbed layer have the same density and modulus as the rigid polymer film, due to energy dissipation effects. For the case of additive adsorption this assumption becomes dubious, and therefore the results are presented in terms of the frequency shift, with the understanding that this is proportional to the total adsorbed layer mass. In addition, it has been demonstrated that the measured frequency shift results in an overestimation of the adsorbed additive mass. This is attributed to water that is hydrodynamically coupled to the additive due to hydration of the adsorbed layer.

Results for the kinetics of adsorption of several additives to the 193 nm bilayer resist are shown in Figure 3. The scale in the frequency shift axis has been adjusted so that a valid comparison between the QCM and SE techniques can be made for the adsorption of polyelectrolyte material. Even if it is impossible to determine the actual mass of the adsorbed layer, the excellent agreement between the QCM and SE traces (except for the initial jump in the SE signal due to the additive injection), imply that the

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temporal evolution of the adsorbed layer has been properly captured. Among the range of additives evaluated, the kinetics of adsorption are reasonably 'fast', addressing any throughput concerns in the manufacturing process. It is also observed that the ionic materials (additives A-C) exhibit a larger frequency shift compared to non-ionic surfactants (additives D-F), suggesting that a significant amount of water might be accompanying the additive adsorption process.
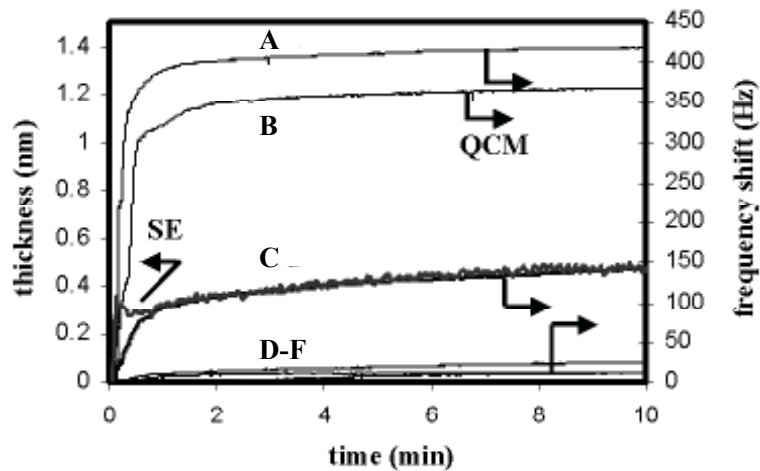

Figure 3. Additive adsorption measured by QCM (frequency shift) and SE (thickness) on 193 nm bilayer resist. A- Anionic surfactant; B- Anionic surfactant/polyelectrolyte blend; C-polyelectrolyte; D-F Non ionic surfactants.

It is unknown whether the additive uptake is only due to surface adsorption or additive penetration into the resist film. A method used to decouple both effects is based on the fact that additive adsorption occurs solely at the resist surface, whereas the mass of additive diffusing into the film is a function of thickness. Figure 4 demonstrates the frequency shift as a function of resist thickness for the 193 nm bilayer resist with an anionic surfactant. It can be seen that there is a linear trend between frequency shift and

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resist thickness, as expected. Furthermore, in the limit of zero thickness there is a considerable frequency shift, which indicates that a large portion of the measurement is due to additive adsorption rather than penetration.
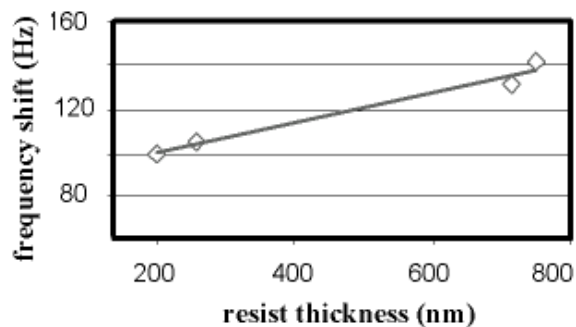

Figure 4. Frequency shift as a function of resist thickness for the adsorption of a polyelectrolyte rinse solution onto a 193 nm bilayer resist.

3.3.3 Interfacial forces between additive-adsorbed surfaces

The interfacial forces that have to be considered in order to understand the stabilization of defects in aqueous solution mediated by an additive-containing rinse can be understood by probing the presence of surface interactions between a test probe and a resist film. AFM (force mode with liquid cell attachment) can be used to verify the existence of such forces by allowing the simultaneous adsorption of the rinse additive to the SiN surface of the AFM tip and to the resist surface. The adsorption of ionic surfactants to SiN surfaces is expected to occur in a similar fashion compared to a resist surface[12,13], with the hydrophobic tail attached to the substrate and the ionic head exposed to the polar liquid environment, so that the energy of the system is minimized.

Force measurements were obtained by recording the deflection of the free end of the AFM cantilever as the fixed end is extended towards and retracted from the sample. In the case where no additives are present in the liquid environment, attractive forces present between the SiN tip and the photoresist surface are readily probed. When an additive-containing rinse is used as a liquid medium, adsorption of the additive to the SiN and photoresist film leads to the appearance of repulsive forces between the AFM tip and the resist surfaces. Figure 5 illustrates the characteristic AFM cantilever deflection created during a force curve measurement under both scenarios.
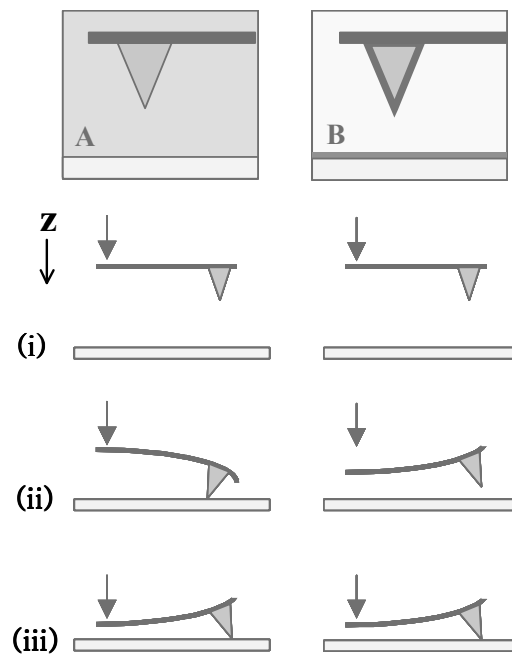

Figure 5. Top: Schematic of the AFM tip-resist surface interaction experiments performed in liquid environment in the absence (A) and in the presence (B) of a rinse additive. Bottom: Characteristic tip deflection during the different stages of the tip approach to the photoresist surface. i) Tip is too far away from the surface and no surface forces are sensed. ii) Tip deflects according to the nature of the surface interactions, either attractive (left) or repulsive (right). iii) Tip goes into 'hard contact'. Mechanical deformation varies linearly with tip displacement in the vertical direction.

The materials used to evaluate the effect of additive adsorption on surface interactions were a 193 nm bilayer resist and a non-ionic polymeric surfactant (0.1 % by mass). Figure 6 shows the characteristic curves obtained for the approach of the SiN tip to the resist surface in the absence and presence of additive.
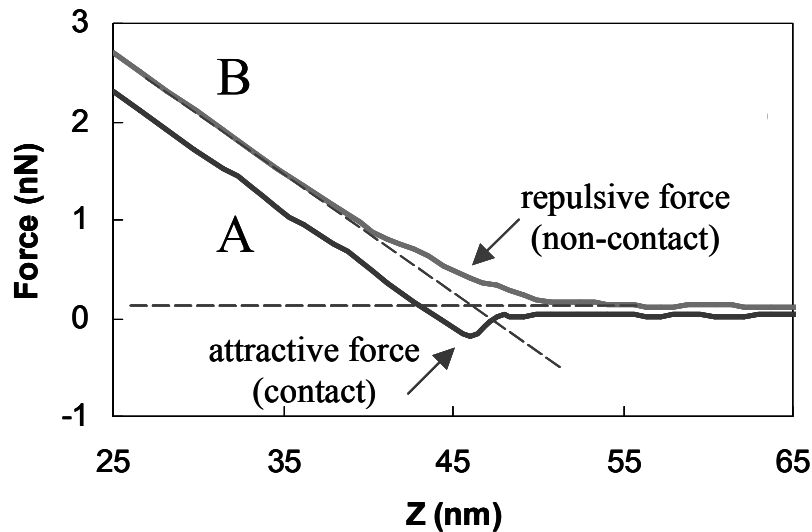

Figure 6. Force curves obtained in liquid media for the interaction between the AFM tip and a 193 nm resist bilayer surface. (A) DI H_2O medium; (B) non-ionic polymeric surfactant (0.1 % by mass).

A small attractive force (curve A) between the SiN tip and the 193 nm bilayer resist was detected in the case where no additive was used. This weak interaction evidenced by a positive deflection of the AFM tip was either absent or extremely faint at times during the force curve measurement. When an additive was incorporated to the aqueous solution, the tip deflection before contact with the resist film was always negative indicating the existence of repulsive forces between the additive-coated surfaces (curve B).

3.3.4 Determination of residual additive after DI water rinse

The adsorption of additives contained in the rinse conditioner can affect the surface energy of the treated photoresist even during the final DI water rinse, if such adsorption process is non-reversible and residual additive is not able to desorb from the resist surface. The practical consequences of a reduced contact angle between the resist sidewall and the rinse liquid during resist processing will be discussed in the next Section.

The presence of chlorine (Cl) and nitrogen (N) in the organic salt additive facilitates the search for residual additive by surface analysis of resist samples using TXRF and NEXAFS, respectively. TXRF[14] is particularly sensitive to higher Z elements, while the NEXAFS signal measured in these experiments arises from the partial electron yield (PEY) of the measured N absorption edge, which is proportional to the N content. The experiments consisted of rinsing blanket resist surfaces with TMAH 0.26 N, followed by the organic salt-containing solution, a DI water rinse and finally drying the treated surfaces. A control sample consisted of either resist films without further treatment (TXRF) or a TMAH-treated resist surface rinsed with DI water (NEXAFS). This distinction between the two techniques was necessary in order to consider the contribution to the N signal arising from the TMAH treatment when using NEXAFS.

The TXRF data shown in Table 7 show some background Cl level on the control sample. For the rinse additive-treated samples, slightly higher Cl counts compared to the control sample were detected, but no clear dependence on the concentration of the salt was observed, suggesting that additive traces remain in the film as the final rinse is not able to remove all the salt.

Table 7. TXRF data for the residual surface concentration of organic salt additive on resist #1. Typical Cl background on bare silicon surfaces was $(50 - 100) \times 10^{10}$ Cl atoms/cm^2.

Rinse additive (% mass)	Cl concentration (10^{10} atom/cm^2)
0 (control)	395 ± 58
0.01	444 ± 73
0.1	465 ± 56
1.0	449 ± 51

NEXAFS results indicate that a resist surface treated with 0.26 N TMAH and an undeveloped control film (data not shown) were identical with background levels of nitrogen (Table 8). However, the relative amounts of N quantified by the PEY are larger for the partially exposed film, indicating that the level of salt remaining on the deprotected film is higher compared to the unexposed resist surfaces.

Table 8. NEXAFS data for the residual surface concentration of organic salt additive on resist #1. Partial Electron Yield (PEY) measured at the N edge is proportional to the Nitrogen surface concentration.

Resist Processing	PEY (N edge)	
	Unexposed	Exposed
TMAH 0.26 N	0.006	0.007
Additive Rinse	0.017	0.048

The total extent of enhanced additive concentration is increased by $\times 2.8$ factor after exposure indicating the increased affinity for the resist. Since the deprotection will increase the concentration of more polar acrylic acid (AA) groups in the resist, an

association between the additive-AA groups may be the source of enriched content at the interface. It is unclear if this enhancement of additive is due to the increased surface concentration, or due to increased depth with which the additive can penetrate.

In order to investigate the change in resist surface energy induced by residual additive, contact angle measurements were conducted on a single layer 193 nm resist system (resist #1) treated with the organic salt additive and a polyelectrolyte[§] additive, separately. Unexposed resist films were immersed for 60 s in the selected rinse additive solutions and subsequently washed with DI water for the same period of time, and dried.

The contact angle for the organic salt-treated surfaces remained unchanged (77° ± 1°) after thorough rinsing with DI water, with respect to the untreated surfaces, suggesting that the trace concentration of organic salt that was left on the resist surface, as detected using TXRF, is too low to effect a change in the resist surface energy. However, the polyelectrolyte solution was able to induce a sharp drop on the resist-water contact angle, as it is shown in Table 9. This finding suggests that the polyelectrolyte interacts strongly with the resist surface, and the adsorbed material cannot be effectively desorbed.

Table 9. Contact angle between resist #1 and water after resist surface treatment with polyelectrolyte additive (60 s), rinsing with DI water (60 s) and drying.

Rinse additive (% mass)	Contact angle
0 % (control)	77°
0.025 %	62°
0.1 %	56°

[§] Unfortunately the atomic composition of the polyelectrolyte additive did not differ significantly from the 193nm resists studied, so surface analysis using NEXAFS or TXRF was not possible in this case.

4. DISCUSSION

4.1 Rinse additives for LER reduction

The reported decrease in LER and surface roughness mediated by the use of an organic salt-containing rinse does not comprise any noticeable change in the overall pattern shape or a significant variation in the average feature linewidth, indicating that no macroscopic flow or removal of resist material appears to be involved during the line edge smoothening process. Instead, the effect caused by the rinse additive appears to be localized at the surface of the resist film or pattern. Even if some extent of additive permeation within the resist cannot be discarded, it is apparent that only resist surface asperities are susceptible to the presence of the additive. A plausible explanation for the observed decrease in LER and surface roughness can be drawn by considering the large interfacial area of each edge protrusion or surface asperity. Roughness suppression can only occur if the polymer chains comprising those asperities are sufficiently mobile. If that is case, partial polymer relaxation driven by the Laplace pressure (surface energy minimization) can induce a leveling effect on protrusions below a certain length scale. This process is opposed by the polymer viscosity, which is expected to dominate in the case of a rough resist pattern or film immersed in DI water. However, the presence of a suitable additive in the rinse can lead to an enhanced polymer surface mobility, which can be the result of partial additive-resist intermixing at the interface and surface plasticization. Such effect would naturally lead to smaller protrusion amplitudes and therefore decreased edge or surface roughness. This does not imply the relaxation to a zero rms roughness but rather to the extent defined by the spectrum of capillary waves of

surface fluctuations[15]. Similar to our findings with additive-containing rinses, the temperature-driven enhanced relaxation of surface polymer asperities has been studied by Kerle *et al.*[16] near the glass transition temperature for the cases of nanoscopically roughened model polymeric films. A temporal evolution of thermally annealed asperities was described, which agrees with the time dependence found in this work for the reduction of surface roughness by rinse additives. Also, Wallace *et al.*[17] detected a faster chain relaxation dynamics at the surface (*ca.* top 5 nm) of polystyrene films compared to the bulk below the glass transition temperature, which supports the interfacial character of the surface roughness reduction process.

The decrease in surface roughness induced in partially exposed films appears to be in agreement with the magnitude of LER reduction found in resist lines. Since typical surface roughness values investigated in this work are in the range of characteristic sidewall roughness values of patterned 193 nm photoresists (2 nm to 5 nm rms)[18], AFM data from additive-treated rough resist surfaces can provide a better understanding of the topographic changes occurring at the sidewall of patterned resist structures during the rinse process. A comprehensive description of the morphological surface changes occurring during the rinse conditioning process and its characteristic length scale will be the subject of a future report.

Alternative processing techniques that can induce LER reduction in resist lines include sonication of the developer solution[19], post-development hard bake cure[20], application of an overcoat layer to the resist[21], heating of the patterned structures combined with exposure to a vapor[22], cross-linking of a filler applied to the patterns[23] and addition of organic salts to the developer solution[24], among other techniques. With

respect to this last example, our results indicate that additives incorporated into the developer are capable of achieving a LER reduction comparable to that attainable by additive-containing rinses, however at the expense of a more pronounced departure from targeted CD values. This observation supports the concept of using alternative processing methodologies that do not compromise other important parameters when incorporated at the end of the process-of-record recipe.

4.1 Rinse additives for defectivity reduction

The concept of additives to the final rinse solution has also proved useful for the reduction of resist defectivity, as it was demonstrated in the previous Section. The defect source in our experiments was in most cases non-specific, and a detailed defect classification was not the objective of our study. However, one particular defectivity source that was present in our experiments is the tendency of some resist systems to form so called 'satellite spot defects'. These defects are typically composed of aggregated photoresist material re-deposited on the substrate surface during the development and rinse step. The source of such defects has been loosely attributed to the formation of retained water spots that locally limit the dissolution and to the gelation-coagulation of partially exposed resist in the developer solution[25,26], as well as to the abrupt pH change introduced by the DI rinse at the time of removing the developer puddle.[27] For the 193 nm bilayer resist studied in this work, this was the main source of defectivity encountered.

The repulsive forces that have to be considered in order to understand the stabilization of resist aggregates in aqueous solutions are dependent on the specific

surface chemistry of the polymer particle and the type of additive used. Electrostatic effects (due to the presence of charged groups, as found in polyelectrolytes and ionic surfactants) involve the ionization of material adsorbed to the polymer surface and the induced electrostatic double layer. Steric stabilization (non-ionic polymeric additives) comprises the screening of the particle core by the adsorbed polymer, which keeps the particles sufficiently far apart so that the attractive van der Waals' interactions are not strong enough to cause aggregation. In this case, particle separation upon adsorption is sustained by to the osmotic repulsive force created due to the unfavorable entropy associated with compressing the polymer chains of the adsorbed non-ionic additive.[28] The existence of such repulsive forces supports the decreased defectivity observed for patterned resist structures, in particular for the 193 nm bilayer system. Aggregates formed during the transition between the development and the rinse step that could potentially precipitate and stick to the unexposed resist or a BARC substrate are stabilized in the rinse solution by the repulsive forces created by the additives.

An effective defectivity reduction process mediated by the use of additive-containing rinses requires the adsorption of the additive to the potential defect and the resist surface simultaneously, followed by the creation of repulsive forces between the additive-coated interfaces. These fundamental processes have been investigated in detail in the previous Section. The fast adsorption of a variety of rinse additives to a 193 nm bilayer resist was detected using QCM, while the presence of repulsive forces between additive-coated SiN and resist surfaces was readily sensed using AFM. The fact that charged polymeric additives are able to easily adsorb both to organic and inorganic surfaces and are capable of displaying both defect stabilization mechanisms described

above[29] suggests that the use of polyelectrolyte-containing additives are able to provide a generalized defect reduction for a variety of resist systems, as it is found in this work (see Table 4).

Once the application of the surface conditioner solution is completed, the additive used to improve the image integrity of the patterned resist film must be removed from the wafer surface, in order to prevent the deposition of solid material upon spin-drying. Therefore a final DI water rinse is necessary to displace the surface-conditioner rinse. In the case of the organic-salt containing rinse studied in this work only trace concentration levels were found at the resist surface, which were too low to alter the contact angle between the DI water rinse and the resist. However, for the polyelectrolyte-containing rinse a marked decrease in the contact angle was noticeable, even after rinsing with copious amounts of DI water. The tendency of certain polyelectrolytes to remain strongly adsorbed to polymer surfaces has been previously identified[30] and it has been attributed to the low probability of every adsorption site in the polyelectrolyte chain to desorb at the same time. Instead, the mobility of the monomer units that do desorb is restricted by the remainder of the polyelectrolyte chain, so those monomers are forced to localize near the surface, thereby enhancing the probability of readsorption. The desorption kinetics of the polyelectrolyte layer from the surface during rinsing with DI water can only be probed by further experimentation. Nevertheless, a reduced contact angle during the final DI water rinse can have and adverse impact on a different image integrity aspect of resist processing, such as a weakening effect on the mechanical stability of high-aspect-ratio densely-packed resist lines. A decrease in the contact angle can lead to an *increment* of the capillary forces acting on the sidewall of patterned resist structures, which can result

in the loss of focus window due to increased pattern collapse[31]. These capillary forces are proportional to the [$\gamma . \cos \theta$] product, where γ is the surface tension of the final rinse fluid and θ is the contact angle between such fluid and the feature sidewall. While a *reduction* on the capillary forces acting on the walls of patterned resist structures during the drying of the rinse liquid can be achieved by incorporation of a suitable surfactant to the final DI water rinse[32], the existence of formerly adsorbed additive material on the surface of pattern structures could easily abate the beneficial effects of a surfactant-containing rinse additive used for this purpose. A method to effectively remove strongly adsorbed material from a previous rinse step might therefore be required.

4. CONCLUSIONS

A generalized post-processing method based on the use of additive-containing rinses that improves the image integrity control of photoresist features was demonstrated. Specific surface-active materials incorporated to the rinse step are used to achieve a reduction of resist LER and a decrease of defectivity levels during resist patterning. In addition, fundamental studies on the interactions present at the resist-rinse liquid interface were carried out in order to understand the underlying mechanisms leading to image integrity improvement. In the case of additive-containing rinses used to control LER, enhanced polymer relaxation occurring at the surface of resist asperities was proposed as the fundamental process leading to improved edge roughness. When a separate group of additives was studied based on their ability to reduce defectivity levels, resist-additive interactions characterized by additive adsorption to resist or foreign material, followed by

the creation of repulsive forces between additive-coated surfaces, was postulated as the enabling mechanism that prevented the aggregation and deposition of potential defects.

From a practical point of view, the implementation of a rinse additive solution for LER and/or defectivity control can be easily introduced in a semiconductor manufacturing process by using existing hardware dedicated to the dispense of surfactant-containing rinses used for pattern collapse prevention. The main advantage of these surface-conditioning rinses is that they usually consist of a short step that quenches the development process and is followed by the final DI water rinse, therefore having a minimum impact on throughput.

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