Patterning Material Challenges for Improving EUV Stochastics

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As the industry looks to extend single-expose extreme ultraviolet (EUV) lithography, stochastic effects become a significant concern to enable yield. Multiple previously-published reports have shown a strong tradeoff between resist sensitivity and observed stochastic defectivity. However, the limits of this trade-off between improving stochastics-related defects with a higher dose resist remains to be understood. How strongly does the resist formulation itself contribute to stochastics, or is it a purely dose-driven effect? Due to the thickness decrease in the patterning stack, the interfacial effects of the resist and hardmask films play a dominant factor in the material stochastics. This offers an opportunity to think differently about underlayer design for sub-32nm pitch patterning. The choice of hardmask can be used to modulate post-litho defectivity to mitigate the stochastics effects and enable more efficient pattern transfer. This paper will address multiple approaches to improving the materials stochastics through resist component optimization and hardmask film development. The defectivity at post-exposure and post-etch are correlated to electrical yield to validate the evaluation. The relative merits of patterning a chemically amplified organic resist directly on an inorganic hardmask or having different types of organic adhesion promoters as an intermediate layer will be also be presented.

Keywords: EUV stochastics, EUV resists, Hardmask, EUV single exposure, EUV defectivity

1. Introduction

As the semiconductor industry makes progress towards high volume manufacturing with extreme ultra violet (EUV) lithography, its second node development of single expose patterning is a key focus. The first node of single expose patterning at 40/36nm pitch has been successfully demonstrated by various teams including our own [1-3]. Due to the significant investment in EUV infrastructure by semiconductor manufacturers, there is a consolidated effort to drive the single expose limit to another node. The pitch and critical dimension (CD) dependency of stochastics defects was shown to increase by orders of magnitude as we scale below 32nm pitch [4,5]. The stochastic variability in each step of the lithography process remains to be the critical challenge that needs to be addressed to enable EUV adoption for manufacturing.

Stochastic effects defined as random variations have been the focus of EUV patterning development in the recent years [6]. The number of EUV photons for a target dose is scaled by a factor of fourteen as we scale the wavelength from 193 nm to 13.5 nm [7]. In this case even a difference of a single photon can induce a significant variability on the effective dose that is delivered to the resist. This is characterized as photon shot noise; ratio of the standard deviation of the number of absorbed photons to the average number of absorbed photons. The relative uncertainty of the number of absorbed photons increases as the number of photons is reduced [8,9].

Relative uncertainty \(= 1/\sqrt{N} \quad (1)\)

In addition to photon shot noise, there are inherent or engineered fluctuations in structure, chemistry, or process event that induces stochasticity to photoresists and the imaging flow. In a chemically amplified resist (CAR), each of the discrete steps such as chemical segregation during
pre-wet and post apply bake (PAB), acid diffusion during post exposure bake (PEB), deprotection and dissolution in aqueous base developer add variability to the process.

The success of single expose EUV patterning is dependent on transfer of the post-litho pattern to the underlying hardmask with minimal amount of defectivity. The most common yield detractors to trench patterning have been identified as nanobridges (where an undeveloped resist area gets transferred and causes a metal line open) and line breaks (where resist lines with thickness differences gets transferred as an open area causing a short in the metal line). Though these types of defects are not new to EUV, their random and non-repeating nature along with the drastic increase of their occurrence dominates electrical yield at the sub 32 nm feature sizes.

The work in this study focusses on mainstream positive tone developed, organic CAR photoresist systems [10]. These photoresists are typically patterned using a multilayer stack that comprises a silicon-based hardmask and an organic planarization layer which assists the pattern transfer to the underlying stack [11,12]. The hardmasks and organic underlayers were developed for planarization and reflectivity control as well as high aspect ratio pattern transfer in sub 100nm pitch DUV patterning. With EUV absorbance being governed by atomic composition [13], and the burden of pattern shrink being placed more at litho than etch, hardmask design and patterning stack definition needs to be optimized for EUV patterning.

The choice of patterning stack and hardmask plays an important role in pattern transfer. At sub-32nm pitch scale, providing a good starting point for pattern transfer with low post-litho defectivity and the ability to tune hardmask etch selectivity to minimize transfer of such defects will require material innovation. Our work focuses on a variety of silicon-based inorganic hardmasks and how they can be used in EUV patterning stacks. The hardmask surface properties are being explored to mitigate nanobridges while the bulk etch selectivity is targeted to tune hardmask open selectivity.

In this paper we highlight our methodology for quantifying stochastic defects. Once a reliable metric that enables comparison of post litho and post etch is established the results are validated through electrical yield correlation [14]. Leveraging this learning vehicle, we present our study on probing the effects of stochasticity in a CAR system to understand the effects of photon shot noise vs material concentration differences. We also explore differences in interfacial interactions by evaluating the modulation of stochastics defects on various substrates.

Our results highlight that even when there is an advantage with respect to photon shot noise with higher contrast (higher dose) resists, increased reactivity in the unexposed area can increase line break stochastics defects. Along with increasing the reactivity in the exposed area, mitigating the reactivity in the unexposed area needs to be considered. Material inhomogeneity can contribute and accentuate this effect at higher dose. The ability to tune the resist hardmask surface is a key factor to post-litho defectivity improvement by increasing the reactivity in the exposed area. This paper will focus on different challenges and potential for innovation for patterning materials as we aim to modulate stochasticity defectivity for EUV single expose extension.

2. Results and discussion
2.1. Characterization of stochastic defects

The characterization of post lithographic defect has been challenging due to the limits of optical contrast. As seen in Fig. 1, optical inspection has no detection sensitivity to both nanobridge as well as line break defects type post litho. Electron beam inspection (EBI) detects line breaks but is challenged with nanobridges. But post etch there was significant contrast for both types of defects using Bright Field (BF) inspection techniques [2,5,15,16]. E-beam and BF inspection was done on HMI ep3 and KLA Tencor 2915 respectively.

![Fig. 1. Post litho defect density at 30nm pitch characterized through optical and e-beam techniques. NB refers to nanobridge defects and OP refers to line break defects. DCD refers post develop critical dimension in the space area.](image-url)
In order to increase the contrast for post litho defectivity using e-beam inspection, different types of conformal coatings were evaluated to quantify their effects for increasing nanobridge capture (Fig. 2). Both silicon and metal oxide based inorganic coatings deposited at room temperature were evaluated and the most sensitive coating for nanobridge capture was downselected to continue this study. We did not see any significant difference between line break capture for each material. The downside of this method was that wafers used for post litho defectivity were sacrificial since the coating could not be easily stripped without affecting the pattern beneath. Coatings that can be solvent stripped without modifying the underlying pattern are under investigation.

Efforts to identify a conformal coating that highlighted the nanobridge without removing or modifying the interface required iterative development cycles and a mature etch process to correlate the trends between post litho and post etch. The correlation also enabled us to verify that post litho defects are real and not artifacts due to the conformal coating. The correlation of the defectivity process window to electrical yield validated this methodology as we were able to quantify the improvements to stochastic defect reduction (Fig. 3).

2.2. Modulation of stochastic defects due to material effects

While the variation due to photon shot noise can be addressed through increasing the number of delivered photons, the effect of material components and chemical processes cannot be easily correlated. The expectation is that as we scale the feature sizes there is a need to increase the number of discrete events in these chemical processes. In the sub 32nm pitch scale where the resist and underlayer film thicknesses are in the 5-40nm range interfacial effects govern these chemical interactions.

As it can be challenging to address the reduction of nanobridges and line breaks simultaneously strategies that can address the mitigation of one type of defect have been explored. With respect to nanobridges, increasing deprotection reactions at the resist and underlayer interface has been a key focus. Designing materials with higher absorbance [17], addition of acid sensitizers [18] acid generating underlayers [19,20] have shown potential for nanobridge defect improvement. For resist line breaks, optimizing its thickness, improving mechanical stability of the resist to withstand local variations and tuning dissolution [21] are being explored. The reduction of one type of defect without impacting the other seems to be the grand challenge for material chemists where chemical mechanisms for their formation could be interlinked.

In this paper, we share a set of experiments performed on a specific CAR system geared toward addressing nanobridge and line break defects to illustrate how they are impacted. The effect of concentration variation, acid diffusion, and interfacial interactions has been the focus of this evaluation. Due to the strong correlation of
stochastics defects on DCD, all samples were targeted for the same DCD range.

2.2.1. Studies with base quencher (BQ) variation

Addition of photo decomposable base has been a significant development in enhancing the resolution of CAR systems [22]. As base quencher component is typically about 5-10 times smaller than that of the photoacid generator, variation of this can induce severe variability to the resist system. We explored this effect through a range of quencher concentrations from 0.5×- 2× with 1× being the reference formulation. The dose increased as expected from 25-100 mJ with increasing base addition. Dose sensitivities were calculated for each sample to ensure that a similar trench DCD range was targeted. The total defect density indicates high level of defectivity for both highest and lowers BQ levels. The trench DCD at defect minima varies between samples which indicates a difference in failure mode (Fig. 4).

Comparison of the nanobridge vs line break defects indicate that the failure mode varies as more BQ is added. At lowest BQ, the dose to DCD target was the lowest and the most dominant defect was nanobridges. This is an expected result when the photon density in the reaction area is low. But as both the BQ composition and dose increases by factors of 1-2× and 2-4× respectively there is a decrease in nanobridge defectivity until it saturates at BQ 1.5×. Line break defectivity shows an increase with higher BQ levels with a slight increase at BQ 1.5× followed by a significant increase at BQ 2×. The line break increase of 100× corresponds to a dose increase of 25mJ between the BQ 1.5× and 2× samples. With higher photons and higher BQ units, BQ 2× showed the highest level of reactivity in the unexposed area resulting in the highest line break counts. We hypothesize that a combination of material effects along with higher photon noise in the unexposed area can account for its increased activity. As BQ concentration reaches above a threshold for uniform distribution, the nanoscopic areas where BQ is high or low could be accentuated with the effect of increased photons (due to higher dose to clear) in the unexposed area resulting in resist thickness loss.

This result supports with the error propagation stochastic model results published by Naulleau and Gallatin that predicts even for an infinitely slow resist (no photon noise), material constraints would still prevent it from meeting the requirement based primarily on the quencher noise [23]. Their model shows that it is not the relative quencher noise that ultimately matters but the growing mean acid count relative to the mean quencher count thus reducing the impact of the quencher stochastics. Theoretically, a resist with no BQ component would be preferred but that would be challenging for a CAR to combat acid diffusion meet its resolution without the aid of a base additive.

2.2.2. Studies with post exposure bake (PEB) variation

Dose to size for this CAR system could be modulated in the range of 46-58 mJ through PEB changes. The slower PEBs afforded higher dose for the same target CD range as expected. Highest PEB and lowest dose has the highest defect density overall (Fig. 5). The nanobridge defects increased for highest and lowest PEBs. For the highest PEB, there will be less photon density in the exposed area due to lower dose. At lowest PEB, though photon density is higher, the reaction density in the exposed area is decreased due to slower acid diffusion. For line break defects, there is a 10× increase compared to the reference for the highest PEB despite lower dose. This could be attributed to the thickness loss in the dark area from higher acid diffusion. But the line breaks in the lower PEB, higher dose areas
don’t increase significantly despite the dose increase due to the slowdown of the reaction kinetics. Along with higher dose, mitigating the reaction density in the unexposed area is key to improving stochastics defects.

### 2.3. Modulation of stochastics defects due to resist hardmask interaction

Post-litho defectivity can be quantitatively measured between different substrates using the conformal coating technique to increase contrast. Though the image contrast will vary depending on different resist and substrate combinations, it allows for initial understanding of how stochastics defects can be modulated based on different stacks [24]. The post litho DCD target for different systems was targeted to be in the same range to compare defectivity on similar trench sizes.

The effect of film composition and functionality on the interface was probed by evaluating different silicon containing hardmasks. The first study was based on different SiN films. SiN deposited with a hydrogen based precursor using PECVD technique was compared with a hydrogen free physically vapor deposited (PVD) film. Comparison of the film structure using FTIR confirmed that SiN with H2 contained NH2 and Si-H functionality while the PVD SiN predominantly contained Si-N bonding [25] (Fig. 6). Both these surfaces were patterned with the same resist thickness post HMDS priming. Post-litho defectivity inspection of these two surfaces showed a high level of microbridges for the SiN containing hydrogen (Fig. 7a). However, the line opens for both surfaces were comparable in the feature size range inspected. The increase in microbridges can be explained with the basic nature of amines; they can deplete acid at the interface that could be otherwise be used for resist deprotection.

![Surface functional group comparison for SiN deposited through PECVD (with H2) and through PVD (H2 free).](image)

**Fig. 6.** Surface functional group comparison for SiN deposited through PECVD (with H2) and through PVD (H2 free).

![Defectivity analysis for PEB variation studies.](image)

**Fig. 5.** Defectivity analysis for PEB variation studies, a) total post litho defect density with e-beam, b) post litho nanobridge defectivity, c) post litho break defectivity.

![Post-litho defectivity readout from e-beam for two different SiN hardmasks patterned with HMDS priming.](image)

**Fig. 7.** a) Post-litho defectivity readout from e-beam for two different SiN hardmasks patterned with HMDS priming. b) Post-litho defectivity readout from e-beam for SiON and SiOC hardmasks patterned with HMDS priming.
This can be further confirmed by looking at the resist sensitivity curves for each substrate (Fig. 8). It is important to note that the top down DCD will be affected by resist profile for each hardmask stack. Photoresists on silicon based hardmasks with HMDS have comparable profile with slight footing so we believe that this comparison is significantly not affected by the profile change for each stack. The SiN with amines requires the largest dose to size for a specific trench size to overcome its basic effect. The effect of amine at the resist interface termed resist poisoning is a well know phenomena in patterning [26]. This case study helps us to confirm its effect in post-litho defectivity to indicate how resist interface can affect the microbridge formation. Priming the surface with HMDS essentially forms a monolayer which enables the resist to be sensitive to surface effects while providing sufficient pattern adhesion.

Another evaluation was done where post-litho defectivity of SiON vs SiOC was compared for films with comparable amounts of nitrogen and carbon (Fig. 8). Both films were deposited through reactive sputtering with nitrogen/oxygen and carbon monoxide/oxygen gas combinations. The target film composition was attained through process parameters such as pressure and gas flow. Both films were deposited in a hydrogen free environment in a low temperature physical vapor deposition chamber. Post-litho defectivity data after HMDS primed litho patterning indicate that the change in film composition from nitrogen to carbon does not have any effect in nanobridge formation. The resist sensitivity graphs also confirm no sensitivity change. Since the post-litho defectivity was not improved by this change, we term this change as a “passive” effect in hardmask. Though a change from SiON to SiOC can have effects in terms of etch transfer for hardmask open, it doesn’t affect the starting point for litho defectivity.

2.4. Active hardmask design

Mitigating post-litho defectivity is a significant challenge for improving post-litho hardmask open defectivity. The previous studies with changes in the hardmask interface indicate that the resist hardmask interaction can be tuned to affect the nanobridge formation without impacting the line break defects. As nanobridges form due to insufficient reaction density at the substrate interface, increasing its acidity can be expected to mitigate it. An extra acid boost can help to increase the number of reactions without the need for extra EUV photons. A hardmask designed with acid content that provide improvements in post-litho defectivity as well as in sensitivity is termed as an “active” hardmask.

Spin on silicon ARC (SiARC) is evaluated as our first active hardmask candidate due to the presence of acid from its thermal acid generator components. Spin on films (SiARC or organic adhesion layers) or grafted organic materials can be designed with acid functionality. These films can be used along with deposited hardmask films to modify the interface with resist. Post-litho defectivity data from a-Si with HMDS vs SiARC substrates indicate that there is potential for improvement in the nanoobridge defectivity (Fig. 9). But for the SiARC evaluated in this study the defectivity improvement is not significant. The line break defectivity of SiARC also seems to be slightly lower when compared with HMDS primed a-Si substrate. We need further characterization of how resist profiles correlate with top down CDSEM measurement to decouple the effects of actual dose needed for a certain physical feature size. The line breaks for passive surfaces with good resist adhesion could result from overdose of the resist profile to attain the same top down DCD as a profile with slight undercut.

Inspecting the higher trench size range highlights another challenge for the active hardmask approach. Acid at the interface causes line collapse due to undercut in the resist profile. This emphasizes the need to balance nanobridge mitigation with pattern collapse. Sensitivity curves on Fig. 10a include a grafted acid layer with about 10× acid compared to SiARC. We have to take into account the difference in rest profiles for underlayers with acidic components (slight undercut) and HMDS primed
2.5. Defectivity and yield correlation

As stochastic defects have been identified as killer defects that limit scaling and manufacturability of EUV, quantification of it plays a crucial role in enabling this technology. E-beam methodology enables us to study post litho defectivity. Bright field inspection grants us a reference point post etch. The correlation of these results is dependent on having a mature etch process that is able to mitigate and translate the post litho defectivity trends post pattern transfer. The ultimate
validation comes with electrical yield readout at different line length macros which helps to quantify the effect of defectivity. This has been a powerful tool to understand how certain material and process parameters can affect defectivity and if the yield is opens (nanobridge) or shorts (line breaks) limited. The case study of BQ variation experiment from section 2.2.1 (Fig. 11), illustrates how post etch results correlate to post litho defectivity results. Post etch defect density is also higher for BQ 0.5× and BQ 2× while the yield for each is limited respectively by opens and shorts. This combined methodology provides a quantitative view of the defectivity process window, with greater insight of the failure mechanisms.

3. Summary

This paper provides insight to probing the stochastics contributions of materials and process effects for a CAR system. Increasing the number of photons to reaction sites has been a major focus for improving EUV stochastics. Hence it is likely to see dose to size increase as we scale to smaller pitches. This study highlights that increasing dose alone will have a limit to stochastic defectivity improvement. Material contributions that govern reaction density in exposed and unexposed area needs to be considered. How the material is designed to have high contrast will determine the stochastic defectivity performance. Even for a non-CAR based metal resist, the material granularity will play a role in stochastics defects [27].

As composition or process changes will be linked to a dose modulation, the defectivity results between dose and material changes can be convoluted. Though increasing the unit concentrations in a multi component system should lead to less variability it will be dependent on the chemistry and miscibility of these materials. Along with the increase in dose that can improves photon related stochastics in the exposed area suppressing reactivity in the unexposed area also needs to be considered. An increase in dose needs to be complemented with an increase in reaction density that necessitates all discrete species of a multi component system to be in close proximity. As demonstrated by our resist-substrate interactions, the chemistry of the interface can play a role in increasing reactivity in the exposed area. Designing CAR systems for better stochastics need to consider material segregation and interfacial effects as these factors govern the variability of reactions in the nanoscopic scale.

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