DSA materials contributions to the defectivity performance of 14 nm half-pitch LiNe flow @ imec

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ABSTRACT
This manuscript shows the relationship between defectivity of a typical chemo-epitaxy sequence and the DSA-specific materials, namely the mat, the brush and the block co-polymer. We demonstrate that the density of assembly defects in a line-space DSA flow, namely the dislocations and 1-period bridges have a direct correlation to certain material-related parameters. The primary focus of this manuscript is on identifying, controlling and reproducing the defects-critical parameters of DSA materials for a stable and low defect performance of DSA flows.

Keywords: Directed self-assembly, chemo epitaxy, defect reduction, DSA materials, Block-co polymer defectivity

1. INTRODUCTION
The patterning capability of directed self-assembly (DSA) using block co-polymers has been well established for over a decade1. Yet, topics such as defectivity control, pattern placement accuracy, cost advantage and ease of integration continue to gate the implementation of DSA in high volume manufacturing (HVM). The capability of DSA, a bottom-up (thermodynamically driven) process to result in a low and stable defect performance has been a subject of intense debate2. Most importantly in this direction, the contributions of the DSA-specific materials – the mat, the brush and the block co-polymer (BCP) to the different defect modes and defect levels have to be understood. This is of utmost importance for achieving stable defect performance as DSA is inherently a materials oriented scheme.

Early reports on DSA defectivity hinted, based on phenomenological observations, a possible relationship between the purity of the block co-polymer samples and the formation of dislocation defects during the self-assembly process3. More recently, L. Williamson et al.4 showed that the (a)symmetry of the block co-polymer composition is a key contributor to DSA defects. We have shown in an earlier report, from a defect source analysis5, that a majority of the dislocation and 1-period bridge defects at the end of the process share common defect coordinates at the mat and the brush layers. This clearly indicated a materials-induced source of defectivity in DSA flows, in addition to the process-related contributions.

In this manuscript, we first focus on defining appropriate splits in the manufacturing process of the DSA materials to identify the defects-critical parameters. We use the process of record (PoR) 14 nm half-pitch Liu-Nealey (LiNe) flow @ imec (Figure 1) to evaluate the effect of the splits on the final process defectivity after pattern transfer into the silicon (Si) substrate.
2. MATERIALS AND METHODS

2.1 Materials

Cross-linkable poly(styrene) (XPS, AZEMBLY™ NLD128), hydroxyl-terminated poly(styrene-random-methyl methacrylate) (P(S-r-MMA)-OH) brush (AZEMBLY™ NLD127), and poly(styrene-block-methyl methacrylate) (PS-b-PMMA, AZEMBLY™ PME312) BCP with \( L_0 = 28 \text{ nm} \), were synthesized by EMD Performance Materials and were used as received. ArF immersion photoresist AIM5484 used for pre-pattern exposure was purchased from JSR Micro. Organic solvent RER650 used for edge bead removal of DSA materials and brush rinsing was obtained from Fujifilm and the photoresist strip chemistry, Orgasolv STR 301™ was obtained from BASF.

2.2 Process flow

The process used for this experiment is based on our previously reported method for the fabrication of chemical nanopatterns\(^5\). All processing was performed at imec on a TEL CLEAN TRACK™ LITHIUS Pro™ Z system. Pre-pattern with a pitch of 84 nm were exposed using an ASML NXT:1950i scanner at 1.35NA using quadrupole illumination (XY polarized, \( \sigma_o=0.87, \sigma_i=0.72 \)). A SiN antireflective coating (ARC) layer of 13 nm was deposited by chemical vapor deposition (CVD) on p doped 300 mm Si substrate. The XPS film, with a target thickness of 7 nm, was spun and annealed at high temperature for 5 min under a \( \text{N}_2 \) atmosphere.

After resist coating and exposure using vendor recommended settings for post-apply bake (PAB), post-exposure bake (PEB), and development, lines and spaces of 84 nm pitch and critical dimension (CD) of 38 nm were obtained. \( \text{O}_2 \) and \( \text{Cl}_2 \) plasma etch was used to trim the resist to target 17 nm CD and to remove the XPS in the trenches. The remaining resist was stripped at room temperature with Orgasolv STR 301. The P(S-r-MMA)-OH brush was spun and annealed for 5 min at 250°C in a \( \text{N}_2 \) atmosphere. Non-reacted brush material was rinsed with RER650. The PS-b-PMMA BCP was coated on the chemical patterns and annealed at 255°C in a \( \text{N}_2 \) atmosphere for 2.5 hours. Defect inspection was done in KLA-Tencor’s 28xx platform and a subsequent scanning electron microscope (SEM) review was performed in KLA-Tencor’s eDR7xxx platform.
2.3 Metrology

For defect inspection, the tool utilized in this study is a broadband plasma optical inspection system (28xx). This is a widely adopted tool for both R&D and production monitoring inspection applications. The initial setup of the tool (wavelength, apertures, modes etc.) was done based on the results of a proprietary offline simulation methodology from KLA-Tencor, which uses a Rigorous Coupled Wave Analysis (RCWA) method to solve the EM simulation. Directed Self Assembly, being a new generation lithography process, the critical defects of interest (such as dislocation and 1-period flat bridges post-Si etch) were first studied by simulations to determine the optimal optical settings to maximize signal. The recipe was then verified and further optimized to maximize sensitivity to all defects of interest whilst suppressing potential noise sources.

3. RESULTS AND DISCUSSION

3.1 Impact of BCP on bridge defects

An initial screening experiment was conducted to identify the most defects-critical material among the mat, the brush and the BCP. Two different batches (gallon) of each material - mat (‘X1’-nominal and ‘X2’), brush (‘N1’ and ‘N2’-nominal) and BCP (‘B1’ and ‘B2’-nominal) were prepared by EMD Performance Materials and were used as-received. Different combinations of these materials were used in the PoR LiNe flow. The final defect density (after Si etch) is taken as the figure of merit to judge the impact of the splits. Figure 2 summarizes the results of this first study.

From this experiment, it was evident that as long the BCP batch B1 was used, the defect density was constantly high. The high defect density primarily resulted from a high density of 1-period bridges as seen in the SEM images in Figure 2. When the BCP batch was switched to B2, the defect density showed a 1000x decrease. The main difference between the two BCP batches, B1 and B2 is in one particular parameter (parameter ‘A’) in the BCP manufacturing procedure. The parameter ‘A’ of B1 was 1 order of magnitude higher than that of B2. This was a clear indication that the quality of the BCP, especially the parameter ‘A’ was critical for the bridge defects. The techniques for controlling parameter ‘A’ are developed and are now implemented as standard practice by EMD Performance Materials for BCP manufacturing.

In order to confirm this hypothesis of parameter ‘A’ in B1 batch leading to bridge defects, the B1 BCP batch was tested with other brush batches (N3 and N4) and in parallel, these brush batches were tested with other BCP batches (B3 and B4). Additionally, the different BCP+brush combination wafers were annealed in two different N2 hotplate modules (H1 and H2) to rule out any hardware-related root cause of this unprecedented density of bridge defects. The results of this experiment are summarized below in Figure 3.

Figure 3 clearly shows that the BCP batch B1 contributes to a marked increase in the density of bridge defects compared to the other batches (B3 and B4) with controlled and lower parameter ‘A’ than B1. This confirms the relationship of parameter ‘A’ to the bridge defect density.
3.2 Impact of BCP and brush on dislocation and bridge defects

To understand the effect of the BCP material parameters on dislocation defects, BCP formulations B3 and B4 with controlled parameter ‘A’ were subjected to defectivity test and used in the PoR LiNe flow in combination with two nominal brush batches (N3 and N4). The results of this study are summarized below in Figure 4.

This study clearly indicated that for the density of dislocation defects, the combination of BCP+brush materials is important. The combination of batches B3+N3 gave the least density of dislocations. The density of dislocations was higher with the material combination B3+N4 and the highest with B4+N4. This suggested that a co-optimization of BCP and brush was critical for an optimal defect performance. At this point however, it is not very clear which material parameter(s) exactly contributed to this trend as the initial chemical analysis of BCP batches B3 and B4 revealed no significant difference. This pointed out that there were more parameters in the materials apart from parameter ‘A’ that need to be understood and controlled for an optimal defect performance.

To understand the effect of the brush-related material parameter(s) towards the defect performance, 6 batches of brush materials with incremental change in the hydrophobicity of the brush (within the range that allowed perpendicular BCP assembly) were synthesized and used in the PoR LiNe flow process. The results from this study are summarized in Figure 5.
The above plot shows that when the brush material is rather on the hydrophilic end, the assembly results in a staggering amount of bridges even in a random SEM image. As the hydrophobicity of the brush increases, the assembly performance reaches an optimal point (at the PoR value) and a further increase results in a rapid increase in registration defects. This shows that hydrophobicity control in the brush layer is important for controlling the assembly defects, the dislocations and the bridges.

In order to understand the material-based root causes of dislocations and bridges in the BCP, a detailed split was defined by changing various BCP synthesis/formulation parameters, including the starting polymer material. Each BCP batch was tested individually and their defect performance is reported below.

Figure 5: Impact of the hydrophobicity of the brush material towards the defect performance of LiNe flow.

Figure 6: Defect performance of individual BCP formulations prepared with different raw materials and filtration technique.
The data in the plot above leads us to two major conclusions. (1) A tighter bulk filtration helps reduce the density of all defect modes, especially the bridge defects. (2) All BCP batches prepared from a specific starting polymer ‘C’ consistently result in low (~1 cm⁻²) density of dislocations even with manual BCP coating. This clearly shows the importance of controlling the BCP polymer quality for a low dislocation defect performance.

4. CONCLUSIONS

We have successfully studied the major materials-based root causes for the assembly-relevant defects in a typical chemo epitaxy DSA L/S flow. For controlling the dislocation defects, the quality of the BCP starting polymer plays a critical role. In addition, a tighter bulk filtration approach during BCP product manufacturing process is key for a low dislocation density. The bridge defects are strongly correlated to the parameter ‘A’ appearing in the BCP formulation process. In addition, a tight control on the hydrophobicity of the brush layer is found to be critical to control the bridge and dislocation defects. The tighter bulk filtration also helps in decreasing the bridge defect density, albeit a smaller gain than the dislocations. The quality of the starting BCP polymer was found to have the biggest impact for dislocation defects. Most importantly, we have demonstrated the level of control needed in the synthesis parameters of the DSA-specific materials to achieve stable and repeatable low-defectivity DSA flows. This study clearly indicates that there are no inherent show-stoppers identified in the materials’ contributions to DSA defectivity.

REFERENCES