

Dissolution Behavior of Photoresists: An In-situ Analysis

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The characterization of the photoresist dissolution process after exposure has been continuously investigated in search for possible clues in the development of optimal photoresist materials and processes suit the requirements for next generation lithography. In this paper, an in-situ analysis of the photoresist's dissolution behavior is performed utilizing high-speed atomic force microscopy. Here, the physical changes in the surface of the exposed extreme ultraviolet (EUV) photoresist film is observed in real-time before, during and after the development process. This new information on the actual pattern formation of photoresists provides clues on how to better understand its mechanism and in effect further improve its performance. In this work, a comparison of the dissolution characteristics in terms of EUV photoresist platform (acryl-based polymer and fullerene-based molecular resist) in tetramethylammonium hydroxide (TMAH) developer was performed. Moreover, using the same polymer resist, the dissolution characteristic difference between the TMAH and tetrabutylammonium hydroxide (TBAH) developers was analyzed.

Keyword: EUV, Photoresists, Dissolution characterization, Atomic force microscopy, Developer solution

1. Introduction

Extreme ultraviolet (EUV) photoresist materials and processing are considered as one of the most critical issues in realizing EUV lithography. Extensive research on high-performance photoresist materials [1-2] and lately, improved methods for photoresist processing have been reported [3-4]. One such process that has been gaining attention in EUV lithography in the past few years is photoresist development or dissolution. Along with resolution and sensitivity, line width roughness (LWR) has become a major concern as required fine patterns reach the 22-nm and beyond [1]. The characterization of the photoresist dissolution process after exposure has been continuously investigated [5] in search for possible clues in the development of optimal photoresist materials and processes suited the requirements [6] for next generation lithography.

Analysis methods such as the quartz crystal microbalance (QCM) and dissolution rate monitors (DRM) provide information that help describe or define the changes occurring on the photoresist film during the dissolution process [7-8]. However, until this time, there has been no actual evidence of what actually happens on the photoresist film during this

chemical process.

In this paper, an in-situ analysis of the photoresist's dissolution behavior is performed utilizing high-speed atomic force microscopy (HS-AFM) [9]. Here, the physical changes in the surface of the exposed photoresist film is observed in real-time before, during and after the development process.

A comparison of the dissolution characteristics in terms of EUV photoresist platform (acryl-based polymer and fullerene-based molecular resist) in tetramethylammonium hydroxide (TMAH) developer was performed. Moreover, using the same polymer resist, the dissolution characteristic difference between the TMAH and tetrabutylammonium hydroxide (TBAH) developers [10] is reported.

2. Experimental

2.1. Materials and sample preparation

For these analyses, the positive-tone chemically amplified acryl-based polymer photoresist, Selete standard photoresist 4 (SSR4) and the fullerene-based positive-tone molecular photoresist Selete model photoresist 601 (SMR601) were used

at a film thickness of 60nm [1, 3]. The SMR601 was applied with a 20nm thick organic underlayer. Optimal post application bake (PAB) and post exposure baked (PEB) conditions were applied for both photoresists [1, 3].

For the developer solution, a 0.26N TMAH and TBAH were utilized at a 1/20 diluted concentration to allow a clearer analysis of the dynamic development process at slower development speeds. The wafer samples were prepared using the small field exposure tool SFET (NA = 0.3) [3]. The SFET is linked to a coater/developer track system (Clean track ACT12 by Tokyo Electron) in a chemically controlled environment. The standard illumination condition used for evaluation of photoresist materials was an annular illumination of σ_{outer} 0.7 / σ_{inner} 0.3.

32 nm isolated line (I/L) pattern exposures are made on the 300mm ϕ silicon wafer which is then cleaved to obtain the 2mm x 2mm wafer samples for in-situ analysis.

2.2. High-speed Atomic Force Microscopy (HS-AFM)

Figure 1 shows the HS-AFM system (Nano Live Vision by Research Institute of Biomolecule Metrology Co., Ltd.) used here at intermittent-contact mode. This system is composed of a “sample assembly” where the wafer sample is attached and a “cantilever assembly” where the cantilever and developer solution is set. The HS-AFM system is an extensively improved version of the AFM previously reported [9]. The detailed description of which, are to be published in a separate paper.

All HS-AFM measurements were performed at room temperature.

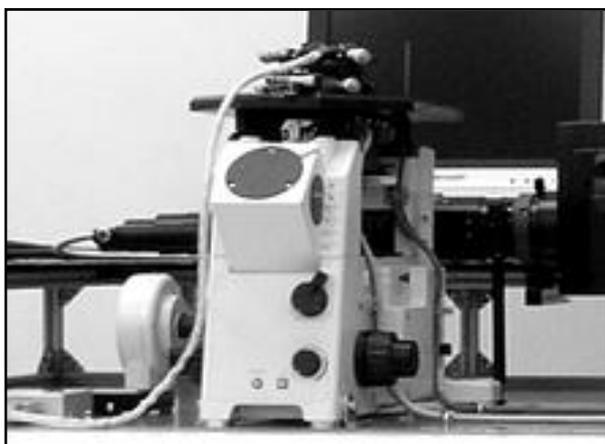


Fig.1 The HS-AFM system (Nano Live Vision by RIBM) used here at intermittent-contact mode.

3. Results and discussion

3.1. Initial analysis results using SSR4

Figure 2 shows the in-situ development analysis top-view results of the 32 nm I/L pattern exposed on SSR4 at increasing arbitrary development time (t_0 - t_{11}). It can be observed that before development at time 0 (t_0), with the wafer sample observed under de-ionized (D.I.) water, some thickness loss assumed to be due to EUV exposure already exists.

As the 0.26N TMAH developer solution is injected into the D.I. water, resulting into a 1/20 concentration, film roughness increase rapidly at the EUV exposed area on both sides of the 32nm I/L pattern from t_1 . At t_2 , the photoresist film starts to swell (increase in brightness which indicates height increase) and continues to increase in size at t_3 and t_4 . The swelled photoresist film, on the right side of the 32nm I/L pattern, breaks (dark spots that represent lower height or pits generated) at t_5 which rapidly spreads at t_6 . At the same time t_6 time line, the photoresist film on the left side of the 32nm I/L continues to swell and breaks, followed by a similar rapid spread on t_7 , allowing the 32nm I/L pattern to manifest. The depth of these EUV exposed areas continues to rapidly increase from t_8 until t_{11} , where the cantilever is assumed to have reached the bottom surface or the silicon wafer. Figure 3 shows the in-situ development analysis results of the 32 nm I/L pattern exposed on SSR4, after three dimensional (3D) rendering.

These results show a clear visual representation of the actual dissolution process. As discussed earlier, photoresist film swelling of the EUV exposed area of the SSR4 was especially significant at t_3 and t_4 (where the swelling overshoots the analysis area’s maximum Z-range). This film swelling is attributed to a significant penetration of the TMAH developer into the acryl-based SSR4 photoresist film.

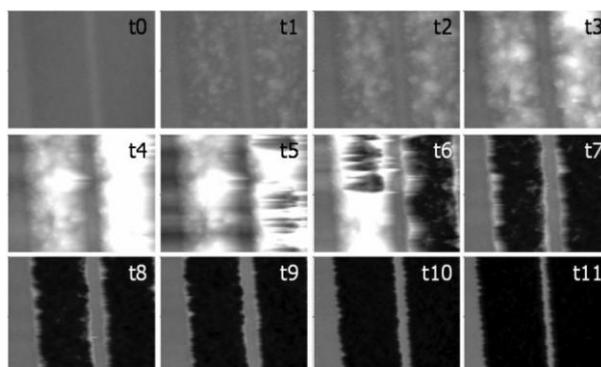


Fig.2 The in-situ development analysis top-view results of the 32 nm I/L pattern exposed on SSR4 at increasing arbitrary development time (t_0 - t_{11}).

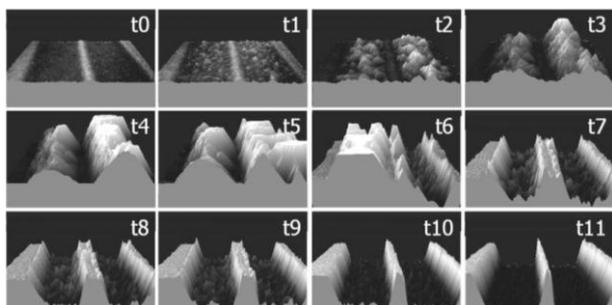


Fig.3 The in-situ development analysis results of the 32nm I/L pattern exposed on SSR4 (after 3D rendering).

Moreover, upon closer analysis of the measured photoresist film at t6 and beyond, a consistent swelling was observed directly on top-corners of the 32 nm I/L pattern. These also provide a clear image of the rapid dissolution of the exposed EUV photoresist film after breaks were generated at both t5 and t6. It is noteworthy that at t7, where the 32nm I/L pattern starts to manifest, some form of film swelling remains on the edges of the protruding I/L pattern. This roughness variation starts to decrease and dissolve between t9 and t11. This variation at the edge of the analyzed pattern shows possible hints in the defining the mechanism of the effect of the development process on the LWR. However, further detailed work is necessary.

3.2. Polymer vs Molecular photoresists

Figure 4 shows the in-situ development analysis results of the 32 nm I/L pattern exposed on both, the fullerene-based molecular photoresist SMR601 and the acryl-based polymer SSR4 photoresist (after 3D rendering).

For the SMR601, there was also some film swelling observed at time t3. However, these were significantly smaller compared to those of the SSR4.

It was also clear that the roughness variation on the EUV exposed photoresist film of the SMR601 was comparatively smaller in grain size and its dissolution is not as rapid as that of SSR4. This difference in grain size is assumed to be due to the difference in molecular size for both acryl-based polymer (SSR4) and fullerene-based molecular (SMR601) photoresists.

3.3. TMAH vs TBAH developers

Figure 5 shows the in-situ development analysis results of the 32 nm I/L pattern exposed on the acryl-based polymer SSR4 at TMAH and TBAH developer solutions (after 3D rendering). Photoresist film swelling due to developer penetration was still observed with the application of the TBAH developer solution.

However, these results show that in comparison to the large bulks of photoresist film swelling observed with the TMAH, the size of photoresist swelling areas for the TBAH were comparatively smaller. This was especially clear at times t3 and t5 where smaller lumps of photoresist film swelling were found. The dissolution characteristics after the swelling area breaks were similar as seen from t7 to t11. It has been reported that with the TBAH developer, lesser penetration into the photoresist film can be expected due to its bulkier molecules [10]. It was also reported that the use of this developer promotes lesser pattern collapse at these small pattern sizes [3].

These results support the assumption that this pattern collapse improvement may have been due to the absence of excessive sizes of photoresist swelling that dramatically dissolve after reaching a certain development time [3].

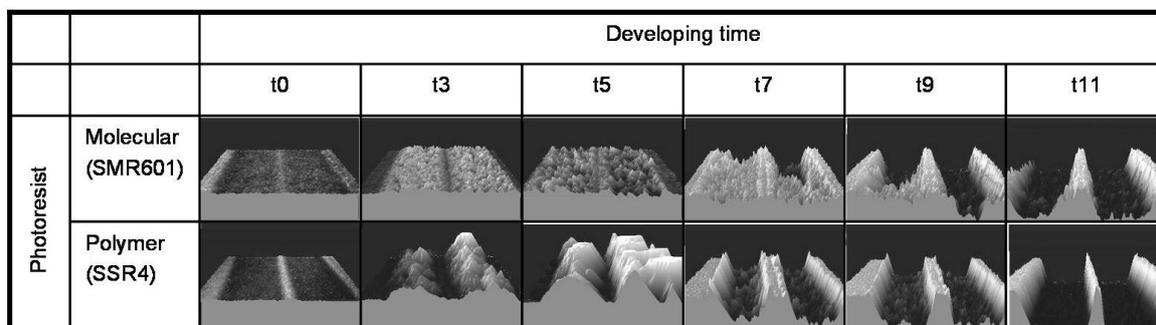


Fig.4 The in-situ development analysis results of the 32 nm I/L pattern exposed on both, the fullerene-based molecular photoresist SMR601 and the acryl-based polymer SSR4 photoresist (after 3D rendering).

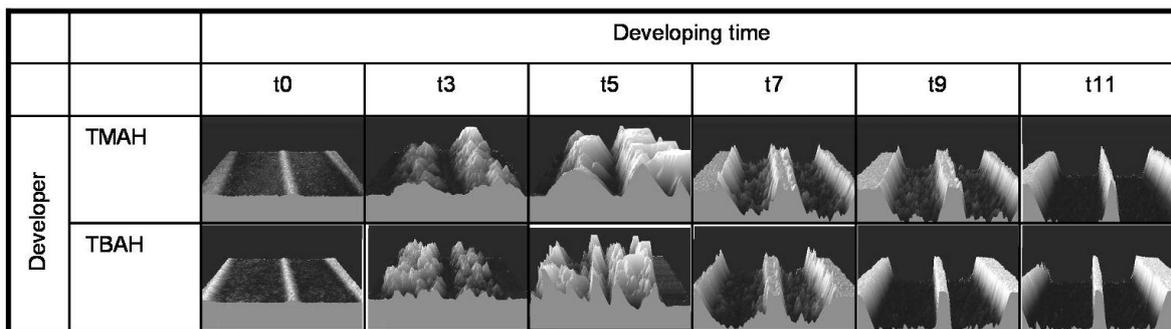


Fig.5 The in-situ development analysis results of the 32 nm I/L pattern exposed on the acryl-based polymer SSR4 at TMAH and TBAH developer solutions (after 3D rendering).

4. Summary

The dissolution behavior of photoresists was observed and analyzed in-situ using the HS-AFM. This work shows that mechanism of EUV exposed photoresist surface swelling during the development process.

A comparison between the acryl-based polymer photoresist and fullerene-based molecular photoresist shows a large difference in swelling characteristics during the initial stages of development. The polymer photoresist showed large lumps of film swelling that rapidly dissolved as development time passes. For molecular photoresists, smaller grains of swelling film were observed and dissolution of the exposed surface was not as fast in comparison to the polymer photoresist. This difference in grain size is assumed to be due to the difference in molecular size for both acryl-based polymer and fullerene-based molecular photoresists.

With the application of the alternative developer TBAH, it was found that the dissolution characteristic of the polymer differs in comparison to the results obtained with TMAH developer. The swelling of EUV exposed film were minimized. This observed as the swelled areas were comparatively smaller with the application of the TBAH.

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