Characterization Studies on Metal-based EUV Resist Film Properties

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Investigations on the resist film depth-profile of a Zr-based EUV metal resist (which contains methacrylic acid or MAA as shell) reveal that the metal cores (Zr) are homogeneously distributed across the film-depth. However, the shell molecules (MAA) in the same resist film have an inhomogeneous distribution (relatively high concentration at the film surface compared to the film bottom). In addition, the total concentration of shell molecules across the film depth is significantly affected (decreases) due to post coating delay and increased exposure dose. Moreover, it is confirmed that the existence of such metal resist film depth inhomogeneities affects the resist's dissolution properties in the developer solution. Specifically, variations in metal resist dissolution characteristics between the film surface, mid-film, and the film bottom are observed. These results confirm the impact of metal resist film properties on its solubility in the developer solution, which can directly affect patterning performance (resolution, line edge/width roughness (LER/LWR), and sensitivity), especially LER/LWR.

Keywords: EUV metal resist, Film depth, Inhomogeneity, *In situ* resist dissolution analysis

1. Introduction

The development of metal-based resist materials (hereafter referred to as “metal resists”) has received considerable research attention [1-18] due to their various perceived advantages for next-generation high-volume manufacturing using extreme ultraviolet lithography (EUVL) [19-23]. Metal resists possess high etching resistance, allowing EUVL application even at thin films. Excellent results have shown that fine patterning, in terms of resolution and line edge/width roughness (LER/LWR), is possible [5]. However, it is apparent that such patterning capabilities come at the expense of low resist sensitivity [5,6,24]. Moreover, recent reports suggest the occurrence of metal resist film instability (at a certain time) after being coated/baked as a film on a substrate (post coating delay or PCD) [1,6-8,10-16,24]. Such issues show that significant research work remains to further improve these types of materials.

In this study, the characteristics of metal resists were investigated focusing on its film properties

(composition/distribution). This was through a film depth analysis/chemical profiling method; a combination of the gas cluster ion beam (GCIB) and time-of-flight secondary ion mass spectrometry (TOF-SIMS) [25,26]. Moreover, to investigate the effect of the metal resist's film depth properties on its solubility in the developer solution, an *in situ* resist film dissolution analysis using high-speed atomic force microscopy (HS-AFM) was implemented [12,27-31].

2. Experimental conditions

2.1. Materials and processing

A metal resist (developed in-house) with a zirconium (Zr) core and a methacrylic acid (MAA) shell was used in these experiments [10,12,24,32, 33]. The film thickness was ~30 nm under a post-application bake (PAB) condition of 80 °C for 60 s. The dissolution process was conducted using normal butyl acetate (nBA) as the developer. This metal resist works as a negative tone type material

when developed in an organic solvent.

Samples for analyses were prepared by coating the resist material on silicon wafers using a spin coater (1H-D7; MIKASA Co., Ltd) and baking them using a hotplate (HHP-401 Shamal; AS ONE Corp.). Film thickness measurements were performed using an ellipsometer (M2000-X by J.A. Woolam Co.).

For some experiments described here, EUV flood exposures were conducted using an open-frame EUV exposure tool (EUVES-7000GC Frame Exposure Tool by Lithotech Japan Corp.), which was equipped with an EQ-10 EUV Plasma Source (Energetiq Technology, Inc.).

2.2. Resist film depth analysis

A combination of GCIB and TOF-SIMS was utilized to analyze the metal resist film depth chemical profile. The GCIB TOF-SIMS analysis method was originally developed as a film depth profiling technique for organic materials, wherein etching incurs very minimal damage to the organic molecules of analyzed films (Ar3000^+ at 5 keV as the sputtering ion). TOF-SIMS analyses were performed using TOF-SIMS 5 (ION-TOF GmbH), which utilized Bi3^+ at 30 keV as the primary (analysis) ion. For these experiments, the GCIB TOF-SIMS was customized for application in metal resist film analysis. Measurements focused on the core (ZrO_2^-) and shell ($\text{C}_4\text{H}_5\text{O}_2^-$) components of the metal resist.

2.3. *In situ* resist film dissolution analysis

The HS-AFM (Nano Explorer or NEX by Research Institute of Biomolecule Metrology Co., Ltd.), originally developed by the Ando et al. [27], was utilized for the analysis of resist film dissolution during the development process in an organic solution. HS-AFM image scanning was performed over an area of $1000 \text{ nm} \times 1000 \text{ nm}$ (400×400 pixels) at an optimized scan rate of $0.5 \text{ frames} \cdot \text{s}^{-1}$. “Biolever fast” cantilevers (BL-AC10FS-A2; Olympus), equipped with carbon nanofiber tips (radius of curvature: $\sim 7 \text{ nm}$), were utilized.

For the experimental procedure using the HS-AFM [12,31], the first step involved searching the in-liquid target pattern (using a pre-dissolution solvent). After determining the exact position of the resist pattern, the developer solution was continuously injected into the analysis area, while the pre-dissolution solvent was dispensed at the same rate (using an auto-inject-dispense module). This enabled continuous and stable scanning of the

pattern surface, even when the pre-dissolution solvent was replaced with the developer solution. However, during this process, the standard developer solution was temporarily diluted, resulting in a slower but clearer observation of the initial stages of the pattern formation process. In addition, the total resist dissolution process was effectively extended in comparison with the typical values used in the actual resist processes.

Fig. 1. Metal resist film depth profile obtained by GCIB TOF-SIMS, wherein the signal intensity of the detected components was normalized and graphed as a function of the film depth, assigning the resist film surface to 0 nm and the resist film bottom to 30 nm depth.

3. Results and discussion

3.1. Resist film depth analysis

3.1.1 Metal resist film depth profile

Figure 1 shows the metal resist film depth profile obtained by GCIB TOF-SIMS, wherein the signal intensity of the detected components was normalized and graphed as a function of the film depth, assigning the resist film surface to 0 nm and the resist film bottom to 30 nm depth. These analyses were performed focusing on the metal core (ZrO_2^-), MAA ($\text{C}_4\text{H}_5\text{O}_2^-$), and the Si wafer (Si^-) as a reference, wherein an increase in detected Si indicated that etching had reached the resist film bottom, i.e., the Si wafer surface. These preliminary results successfully demonstrate the suitability of GCIB TOF-SIMS for obtaining the resist film depth profile of metal resist chemical components.

Based on these results, it is observed that the Zr metal core is evenly distributed from the resist film surface to the bottom. However, the MAA shell molecule concentration decreases gradually from

the resist film surface to the bottom. It is noteworthy that shell molecules are assumed to play an important role in resist film dissolution (higher concentration translates to higher solubility in the developer solution).

3.1.2. PCD effect on metal resist film depth profile

Recent reports on metal resists revealed possible issues in post coating film stability after a certain time (PCD), which affects lithographic performance, e.g., resolution, line edge/width roughness (LER/LWR), sensitivity, and defect generation. Specifically, metal resists, which are typically of the negative tone type, have exhibited deterioration in film solubility (in a developer solution) after a certain time, after being coated to the substrate and baked (PAB).

Figure 2 shows the metal resist film depth profile immediately after compared to 24 h after coating, as obtained by GCIB TOF-SIMS, wherein the detected shell molecules were normalized using the detected core components (shell/core ratio) as a function of film depth.

Based on these results, PCD causes a decrease in the concentration of chemical components detected and assigned as shell molecules that can be observed across the film depth assigning the resist film surface to 0 nm and the resist film bottom to 30 nm depth. Further detailed analysis is necessary to define the specific cause of this decrease in shell molecules after a certain time. However, this decrease in shell molecule concentration is considered as a main factor in the deterioration of metal resist solubility.

Fig. 2. Metal resist film-depth profile immediately after compared to 24 h after coating, as obtained by GCIB TOF-SIMS, wherein the detected shell molecules were normalized using the detected core components (shell/core ratio) as a function of film depth.

3.1.3. Exposure dose dependence of metal resist film depth profile

Figure 3 shows the metal resist film depth profile at specific EUV exposure doses, as obtained by GCIB TOF-SIMS, wherein the detected shell molecules are normalized with the detected core components (shell/core ratio) as a function of film depth, assigning the resist film surface to 0 nm and the resist film bottom to 30 nm depth. These results show that each increase in exposure dose translates to a corresponding decrease in shell molecule concentration across the film depth. Moreover, a similar trend is observed even at increased exposure doses.

Fig. 3. Metal resist film-depth profile at specific EUV exposure doses, as obtained by GCIB TOF-SIMS, wherein the detected shell molecules are normalized with the detected core components (shell/core ratio) as a function of film depth, assigning the resist film surface to 0 nm and the resist film bottom to 30 nm depth.

For negative tone resists, an increase in exposure dose translates to a decrease in film solubility, thereby resulting in the formation of patterns on the exposed areas. The same concept is applied to this metal resist, which is also a negative tone-type material. The exposure dose dependence of shell molecule concentration (as observed in these results) shows just how significant shell molecules and their corresponding film depth distributions can affect metal resist film solubility.

3.2. *In situ* resist film dissolution analysis

To further understand the effect of shell molecule concentration (higher concentration at the film surface compared to the bottom, as described in 3.1.1.) in metal resist film solubility, an *in situ* analysis of metal resist film dissolution in the developer solution was conducted.

Fig. 4. HS-AFM images (birds eye view) obtained defining the metal resist film dissolution characteristics during development in nBA organic solvent, at various points in the dissolution time (s).

Figure 4 shows the HS-AFM images (birds eye view) obtained defining the metal resist film dissolution characteristics during development in nBA organic solvent, at various points in the dissolution time (s). These results show a change in the metal film surface characteristic as dissolution advances.

Specifically, at the early stages of the dissolution process (near the film surface, at 32 s), the resist film surface dissolves smoothly, without significant spatial variations. Notably, during these initial stages of resist film dissolution, resist film swelling is observed (at 34 s). This is characterized by surface smoothing at specific sections, wherein trench-like formations were originally observed (comparison between 34 s and 32 s). This phenomenon that we refer to as “nano-swelling” has been discussed previously [12].

At more advanced dissolution times (mid film, between 36 s and 44 s), non-uniform dissolution is observed, resulting in spatial variations in the form of protrusions (delayed dissolution) and trenches (advanced dissolution). At even longer dissolution times (at 54 s and onwards), most of the resist film is dissolved (bottom of the film), and resist residue is observed, which remains even after much longer dissolution (at 82 s).

The existence of these spatial variations confirms the presence of inhomogeneity in the metal resist film depth profile. Furthermore, it also confirms how such film depth inhomogeneity affects resist film dissolution. The presence of inhomogeneities is

considered detrimental to patterning performance, and as shown here, may also result in the generation of defects such as residues.

4. Summary

Characterization of the resist film properties of a Zr-based EUV metal resist (which a MAA shell) was successfully conducted using GCIB TOF-SIMS and HS-AFM.

The results indicate that the metal cores (Zr) were homogeneously distributed across the film depth. However, for the shell molecules (MAA), an inhomogeneous distribution was observed. In addition, it was also confirmed that the total concentration of shell molecules across the film depth was highly affected (decreases) due to PCD and an increased exposure dose. Moreover, dissolution analysis results showed that such metal resist film depth inhomogeneities caused variations in the material's dissolution properties.

These results provide evidence of the impact of metal resist film properties (inhomogeneity) on its solubility in the developer solution. Metal resist solubility is considered an important factor, which can directly affect patterning performance (resolution, LER/LWR, sensitivity), especially on LER/LWR.

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