Structural Changes of Photoresist on Wafer Studied by Pyrolysis-GC/MS Combined with Micro-GPC

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A novel method for the direct analysis of photoresist pattern was developed on the basis of Pyrolysis-GC/MS combined with micro-GPC. Firstly, a new sampling technique allowed us to collect the surface and the core of the photoresist pattern separately. Moreover, µGPC and Py-GC/MS analyses provide the information for the distribution of resist ingredient inside resist pattern, which includes original polymer, reacted polymer, and photo acid generator through the ArF patterning process. This novel analytical method can provide remarkably helpful information about identifying proper control knobs for lithographic performance of ArF resist and for next generation lithography.

Key words: photoresist, µGPC, Py-GC/MS, LWR

1. Introduction

The scaling of device design will proceed according to the Moore’s law, or more likely to the “More than Moore’s law”. The targeted device design has been reaching down to 20 nm half pitch and beyond [1]. In order to achieve the requirements, multiple next generation lithographic (NGL) processes are under investigation, such as extreme ultra violet lithography (EUVL) [2], directed self-assembly lithography (DSA) [3], nano-imprint lithography (NIL) [4] and so on. Though there are significant progress in NGL processes, these lithographic processes are not mature enough yet and further great deal of development is required for application on advanced device production.

Therefore, the extension of ArF lithography needs to fill gap between current industrial requirement and new lithography process matureness. ArF immersion lithography has been applied for device high volume manufacturing since device critical CD was 4x nm half pitch. In addition, combination of ArF immersion lithography with multiple patterning allows shrinking minimum pattern size pitch division to multiple [5, 6]. For this multi-patterning process, roughness of original resist patterns transfers to patterns after pitch division. As a result, roughness impact on generated patterns increased dramatically. In general, line width roughness (LWR) should be controlled within 10% of the pattern size in order to gain acceptable yield at the device manufacturing. This is a very challenging target from the viewpoint of resist design for supporting 20 nm half pitch and beyond lithographic processes.

Last year we revealed that TOF-SIMS depth profiling using Gas Cluster Ion Beam (GCIB) allowed the ability to clearly identify photoresist ingredient distribution in the photoresist films from the surface to the bottom of the resist films [7]. Although this novel method can be a powerful tool to analyze distribution of chemical components in the resist film, the output from TOF-SIMS principally reflects chemical components almost existing in the top of the resist film or pattern. In other words, we could not distinguish side wall of resist pattern from core of resist pattern, where consists of highly curious chemical species to understand the mechanism of LWR generation.
Thus, new methodology to analyze resist pattern two-dimensionally is required.

In ArF immersion process, resist film is exposed at 193 nm wavelength light through water to generate acid on prescribed area. Next, post exposure bake (PEB) is applied to precede resist polymer’s de-protection reaction to change its polarity for dissolution contrast (Fig. 1). The boundary area between exposed and un-exposed is the primary chemical part to predict LWR formation. In this study, we removed the un-exposed area by organic solvent washing to generate resist pattern without any contamination such as tetra methyl ammonium hydroxide (TMAH) as common developer of lithography. This process allows us to implement precise analysis to know the chemical components on resist side wall.

There are still two major problems to analyze the resist pattern two-dimensionally. Firstly, it is how to collect side wall and core of the resist pattern separately. The other is how to analyze small amount of the collected sample, which is only 1~2 mg from a piece of 300 mm wafer. Among them, for the method of selective collection, we utilized the properties of slow dissolution rate of resist pattern into organic solvent. Finally, un-exposed area was washed out by 4 sec quick contact. Then, we collected materials on resist pattern surface by short soaking time, which are 4~10 sec. At end, the core part was collected by 1 day long soaking (Fig. 2). In this process, we used n-butyl acetate as an organic solvent for selective collection. The pattern was gradually thinning depended on the soaking time (Fig. 3). Thus this method allows us to collect desired resist thickness from pattern surface by changing soaking time. We implemented two-dimensional chemical composition analysis by using this selective collection method. For the trace analysis, on the other hand, we have studied the micro-GPC (µGPC) fractionation followed by MALDI-MS, IR and pyrolysis-GC/MS (Py-GC/MS) [8, 9]. A diagram of the system is shown in Figure 2. It is expected that this system enables us to separate and identify components in a trace amount of sample.

In this study, the Py-GC/MS combined with µGPC fractionation was applied to the structural analysis of the components in resist pattern after immersion lithography.

![Fig. 1. a) optical intensity in L/S pattern, b) protected polymer concentration after PEB in L/S pattern](image)

![Fig. 2. Strategy for selective collection of resist pattern surface and pattern core.](image)

![Fig. 3 CD-SEM images before and after soaking.](image)

2. Experimental

2.1. Photoresist materials

Formulation of photoresist investigated in this study is shown in Table 1. The photoresist was prepared by mixing polymer, PAG, quencher, and
solvents. Protecting group ratio of photopolymer is 60%. The solution was filtered through 0.02 µm PTFE filter prior to the evaluation.

2.2. Wafer preparation

Immersion lithography was carried out on 300 mm silicon wafers using a ACT12/Lithius Pro (coating, baking) and a Nikon NSR-S610C (exposure).

Photoresist was spin-coated over BARC (ARC66, Nissan Chemical Industries) on silicon wafer and baked at 100°C for 60 seconds (PAB, post applied bake) to form a photoresist film 110 nm thick. The photoresist-coated wafers were exposed through a 6% HT mask using three different exposure conditions to print 70nm L/40nmS pattern after first organic solvent treatment. Exposure was done with following 3 illumination conditions. 1st condition was Annular illumination with 1.30 NA, 1.26 iNA, ratio 0.79, 2nd was Dipole illumination with 1.20 NA, 1.1 iNA, ratio 0.78 and V-polarization, 3rd was Quadropole illumination with 1.30 NA, 1.26 iNA, ratio 0.8.

PEB was applied on these exposed wafers at 105°C for 60 seconds. And then un-exposed area was washed out using n-butyl acetate for 4 seconds to obtain desired test pattern. Optimum energy (Ecd) to print 70 nm lines was determined by plotting the critical dimension (CD) values, measured on a top-down scanning electron microscope (SEM) (Hitachi CG4000 CD-SEM). LWR was measured for 70nmL/40nmS pattern. The LWR was defined as 3 sigma of line width distribution.

2.3. Selective collection of resist pattern

A half piece of 300mm wafer (A-1, D-1, and Q-1 respectively) was cut into small pieces. These small pieces were dipped in n-butyl acetate bath (Bath-A) for 10 seconds one by one. And then these pieces dipped in Bath-A were thrown in another n-butyl acetate bath (Bath-B) and stood in Bath-B for one day. n-Butyl acetate in Bath-A and Bath-B was concentrated individually to get dry mixture. Each mixture was dissolved in 2 mL of tetrahydrofuran (THF) and then filtered, followed by evaporation of volatiles. Sample derived from both Bath-A and Bath-B was dissolved in 100 µL of THF respectively.

2.4. Analysis and preparative isolation by µGPC

The equipment was composed of an HPLC pump, a UV-Vis detector and an auto-spotter (AccuSpot, Shimadzu). HPLC grade THF was used as mobile phase. A GPC column (GF310A-1E, 250 mm x 1 mm ID, Shodex, Japan) was used. 2 µL of the sample solution prepared above were injected. Six fractions were collected on each sample cup for Py-GC/MS by spotting eluent every one minute (tR = 7 min to 13 min).

2.5. Pyrolysis gas chromatography/mass spectrometry

The compositional analysis of photoresist was performed by Py-GC/MS system, which consisted of a vertical microfurnace pyrolyzer [Frontier Lab Model PY-2020iD], a gas chromatograph [Agilent Technologies 7890A GC system] equipped with a metal capillary separation column [Frontier Lab, Ultra ALLOY-5 (MS/HT), 30 m x0.25 mm i.d., coated with 5% diphenyl 95% dimethylpolysiloxane (0.25 µm film thickness)] and a mass spectrometer.
[JEOL JMS-Q1050GC] with an electron ionization (70 eV) source. The sample cup containing µGPC fraction was dropped into the center of the pyrolyzer heated at 500°C. The produced compounds in the pyrolyzer were dynamically transferred to a gas chromatograph.

2.6. Simulations
Simulation for optical images was carried out by using KLA-Tencor PROLITH X4.1.1.

3. Results and discussion
3.1. General study
3.1.1. Comparison among pattern wafer and coating-wafer
µGPC measurements of photoresist extracted from photoresist-coated wafer with only film bake process and photoresist-coated wafer with exposure and 4 seconds soaking were carried out. Fig. 4 shows µGPC chromatograms of a) A-1 after PAB and b) A-1 after Soak. On the chromatogram of A-1 after PAB, the peak derived from the photopolymer was observed from \( t_R = 7 \) min to \( t_R = 11 \) min. In the case of A-1 after soak, most of the unexposed polymer was eliminated by soaking, and a broad peak from de-protected polymer was observed from \( t_R = 8 \) min. Small peak around \( t_R = 11 \) min (After Soak in Fig. 4) corresponds to impurity of \( n \)-butyl acetate as a soaking mediate. Strong peaks around \( t_R = 12 \) min were observed both After PAB and After Soak sample. Former one (After PAB) probably corresponds to amine quencher or \( n \)-butyl acetate. On the other hand, later one (After Soak) corresponds to degradation products of PAG, because the compound having a molecular weight of 262 was detected by Py-GC/MS measurement. Fig. 5 shows a reaction mechanism of PAG.

3.1.2. Chemical composition of resist pattern
To compare chemical composition between surface and core of the resist pattern, µGPC measurements of A-1 were carried out. Fig. 6 shows the chromatograms of A-1 collected from a) Bath-A (10s soaking) and b) Bath-B (1 day soaking). The peak intensity of the polymer in A-1 collected from Bath-B was stronger than that of Bath-A, which is consistent with the SEM images (Fig. 3).

Moreover, the relative intensity of the degradation products of PAG (\( t_R = 12 \) min) against the reacted photopolymer was quite different between 10s’s and 1day’s one. Later one was much stronger. In other words, the distribution of the acid generated from PAG correlated positively to the optical intensity (Fig. 1).

![Reaction mechanism of PAG](image)

![µGPC chromatograms of a) A-1 after PAB, b) A-1 after Soak](image)

![µGPC chromatograms of A-1 collected from a) Bath-A and b) Bath-B](image)

Fig. 4 µGPC chromatograms of a) A-1 after PAB, b) A-1 after Soak

Fig. 5 Reaction mechanism of PAG

Fig. 6 µGPC chromatograms of A-1 collected from a) Bath-A and b) Bath-B
3.2 Investigation for relationship among illumination, de-protection reaction, and LWR

3.2.1. Different illuminations and LWR

Lithographic performance with different illumination are shown in Table 3. Fig. 9 shows optical intensity in simple L/S pattern with different illumination conditions. Dipole illumination shows higher optical contrast and results in better LWR than annular and quadrupole.

3.2.2. μGPC analysis of photoresist

Comparison of chemical composition at surface and core of the resist pattern among three illuminations was carried out as shown in Fig. 10 (surface) and Fig. 11 (core). The trend of PAG were calculated by dividing the peak intensity of the protecting group by total peak intensity.

Fig. 8 shows the relative peak intensity of the protecting group in μGPC-fractionated polymer obtained by Py-GC/MS. In this chart, the later the retention time became, the smaller the relative intensity of the peak from protecting group became. This result indicates that not only molecular weight (molecular size) but also polarity of the polymer affects the strength of interaction between polymer in photoresist and stationary phase of GPC column. Furthermore, the relative intensity of protecting group overall was smaller at 1 day soaking than that of 10 sec soaking. Generally, polymer in photoresist around core area of the resist pattern is lower ratio of protecting group than that of surface area. These results clearly indicated that selective sampling method employed in this work was well done and μGPC and Py-GC/MS was suitable for the analysis of photoresist.

Table 3 Lithographic performance of photoresist samples in this study

| Sample name | Photoresist | Illumination  | Lithographic performance at 70nmL/40nmS |
|-------------|-------------|---------------|------------------------------------------|
|             |             |               | Ecd [mJ/cm²]                              | LWR [nm]    |
| A-1         | Resist A    | Annular       | 15.5                                     | 7.0         |
| D-1         |             | Dipole        | 16.0                                     | 5.0         |
| Q-1         |             | Quadrupole    | 13.5                                     | 10.0        |

Fig. 9 Optical intensity in L/S pattern with different illumination.
degradation is quite interesting. In case of A-1 (annular) and Q-1 (quadrupole), the abundance of the degradation product at surface and core of the resist pattern are almost same. On the other hand, the content of the degradation product at surface collected from D-1 (dipole) is less than that of A-1 (annular) and Q-1 (quadrupole). At the core, the content of the degradation product of D-1 was larger than that of A-1 and Q-1. These results clearly indicate that the optical contrast in resist pattern of D-1 (dipole) was higher than A-1 (annular) and Q-1 (quadrupole).

3.2.3. Py-GC/MS analysis of photoresist
Figs. 12 and 13 show the relative intensity of protecting group obtained by Py-GC/MS measurements of pattern surface. Value on the y-axis is the average of each sample.

Among 3 illuminations, the dipole illumination decreased the relative intensity of protecting group in the resist pattern most between surface and core. This means that the resist pattern by dipole illumination had the highest deprotection reaction contrast among these 3 illuminations. This result is consistent with a simulation result in Fig. 9.

Figs. 14 and 15 show the pseudo-distributions of the polymer calculated from Py-GC/MS results of μGPC-fractions with the following expression.
The deprotected photopolymer of pattern surface showed peak shift toward longer retention time. There was no significant difference about shift width among resists of 3 illuminations. On the other hand, the distribution of the polymer in pattern core with dipole illumination (D-1) shifted most in Fig. 15. This means that the extent of deprotection reaction proceeded by dipole condition is the most in these 3 illuminations. These results are consistent with a simulation result in Fig. 9.

3.3 Correlation with LWR

In general, smaller half pitch shows lower optical contrast and results in worse LWR. In this study, A-1 (annular) and Q-1 (quadrupole) showed lower contrast of acid generation and de-protection reaction than D-1 (dipole). Lower the contrast of de-protection reaction obscures the boundary between exposed and unexposed area in the resist film. Obscure boundary resulted in unsatisfied solubility of polymer against organic solvent. Therefore, the LWR of A-1 and Q-1 is supposed to be worse than D-1. In order to obtain better LWR, it is desired to select the photoresist components or illumination which show sufficient optical contrast and sufficient de-protection contrast respectively. Based on the discussion above, this novel analysis of photoresist pattern utilizing μGPC/Py-GC/MS allowed us to visualize photo acid generation reaction and distribution of de-protection reaction of polymer separately. This method will be a quite useful technique for analyzing and designing photoresist materials.

4. Conclusion

A novel analytical method for photoresist pattern was developed on the basis of three important processes.

Firstly, a novel selective sampling method for a resist pattern allowed us to control thickness of the surface to be dissolved in an organic developer by changing the soak time.

Secondly, the distributions of PAG degradation products and de-protected polymer in the photoresist were visualized by μGPC. These distributions reflect the distribution of optical intensity and diffusion of de-protection reaction in the photoresist pattern respectively.

Thirdly, the polymer composition in the resist pattern was analyzed by Py-GC/MS measurements of the μGPC fractions. The ratio of protecting group in the resist pattern is undoubtedly a useful piece of information for resist design. Further study with polymer having different kinds of protecting group or protecting group ratio has been planned as future work.

These achievements allow us to identify proper control knobs for lithographic performance of the photoresist which is remarkably helpful. This novel method can also be a powerful tool not only for extending the ability of ArF immersion lithography, but also for improving and simplifying device production monitoring and photoresist quality control.
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