Dissolution Rate Monitor Tool to Measure EUV Photoresist Dissolution

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The resist development step in photolithography is a complex process involving selective dissolution between exposed and unexposed photoresist. This phenomenon is commonly described by a one-to-one relation between dissolution rate and deprotection level of the photoresist. Experimentally, the dissolution rate can be obtained dynamically via a dissolution rate monitor. In EUV lithography, photoresist films are typically below 50 nm, and total dissolution of the film can be very quick. In this work, we have improved a custom built dissolution rate monitor and developed a procedure to record experimental data on dissolution rate of very thin film of EUV photoresist using multi-wavelength reflectometry. We present the results of the validation of this set-up, which ensures repeatability, good temporal resolution, and a short black-out time. The tool now available proves to be suitable for the study of EUV photoresist dissolution and can provide relevant input for lithographic software and for improving the design of photoresists. The impact of film thickness variation is presented, as well as a comparison of two chemically amplified resists with a different quencher loading.

Keywords: DRM, EUV Lithography, Photoresist, Development, Dissolution

1. Introduction

EUV lithography is going to be introduced in high volume manufacturing of microelectronic devices in the coming years [1]. Yet, important challenges need to be solved as soon as possible to enable this integration. Listed second in the challenges identified at the EUVL symposium 2016 is the need for photoresist to simultaneously meet resolution, sensitivity and roughness targets [2].

Recently there has been good progress in both best resolution and sensitivity, with resolution below 16nm half-pitch at a dose around 20 mJ/cm$^2$ [3]. Nevertheless, roughness is still way above requirement: LWR hardly goes below 5 nm LWR where it should be at 3.2 nm.

Amongst the contributors to this roughness, photoshot noise [4], chemical shot noise [5] and acid diffusion [6] are well documented. Less explored is the development process, playing an important role in roughness formation. Notably, the polymer molecular weight [7,8] and $T_g$ [9], or the choice of developer solution [10] have shown to impact the resist dissolution and as such the roughness of the remaining feature.

To describe the development step, Various models, from simplistic (Ferguson, Mack) [11,12] to more complex (notch, Houle) [13,14], have been proposed. These models are mainly translated in lithographic software as a one-to-one relation between dissolution rate and deprotection level of the photoresist. But experimental data is needed to fit these models for each photoresist. Therefore, appropriate tools are needed to measure the dissolution rate of photoresist films, which becomes challenging for EUV resists as the thickness of these films is decreasing to below 50 nm.

One possibility to study the impact of development is by a static expose-dissolve-measure method, comparing resist feature size and roughness measured after development for wafers processed...
using different development recipes. But in order to get more insight on the photoresist dissolution itself, specific techniques have been developed, allowing the dynamic measurement of dissolution rate of photoresist.

Quartz Cristal Microbalance can be used to record photoresist mass and viscosity changes when in contact with a developer solution [15]. Recently, High-Speed AFM has demonstrated the possibility to visualize dissolution in-situ [16]. But single-wavelength reflectometry remains widely used for dynamic dissolution measurement, as it is available in a commercial Dissolution Rate Monitor tool (by Litho Tech Japan) [17].

Each of these techniques has its advantages and limitations: QCM requires to know the density of the resist (in contact with developer) in order to quantify development rate, and density measurement of very thin organic film can be tricky. Furthermore, this density can potentially change during development (solvent swelling,...). QCM, as HS-AFM, requires to put the film in contact with an inert liquid before switching to the developer solution at the start of the measurement. When the developer is an aqueous solution (typically tetramethylammonium hydroxide (TMAH) at 0.026 N), the corresponding inert liquid is water. But several EUV resists use an organic solvent as developer solution (n-Butyl acetate for example). In this case, it can be difficult to find an inert organic solvent. Furthermore, the switch from this liquid to the developer will happen gradually over a few seconds. Having no clear starting point for the dissolution generates uncertainty on measurement for very fast dissolving resist.

Also, QCM requires specific quartz holders and HS-AFM requires small coupons, so direct measurement on 300 mm wafers exposed on full field EUV scanner is not possible.

Finally, Single-Wavelength DRM tools, as commercially available, were designed for previous generation resists, where film thickness can be as high as a few micrometers. Inherent to EUV photoresist, the film thickness on which we want to measure dissolution rate is in a range between 15 and 50 nm, which can be dissolved in a few milliseconds, requiring a higher response rate and sensitivity.

In order to meet these requirements, a DRM tool using multi-wavelength reflectometry at high acquisition speed has been developed at imec [10], in collaboration with TEL (Tokyo Electron Limited). It is, based on the concept invented by Konnerth & Dill [18] and developed by Sheer et al. [19,20], but adapted to 300 mm wafers and specifically targeting EUV resist thin film.

In the following section, the tool will be described, together with the measurement procedure deployed. Then, the experiments realized to validate the tool will be discussed, and finally results of dissolution of several EUV resists will be presented.

2. Experimental

2.1. Materials

In Table 1, the photoresist used in the three experiments described in this work are presented, together with their processing condition (post application bake (PAB) temperature and time, film thickness (FT), post exposure bake (PEB) temperature and time, and developer solution used.

<table>
<thead>
<tr>
<th>Exp.</th>
<th>Resist</th>
<th>PAB</th>
<th>FT (nm)</th>
<th>PEB</th>
<th>Developer</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.1</td>
<td>NXE1720</td>
<td>110°C</td>
<td>40</td>
<td>/</td>
<td>nBAa</td>
</tr>
<tr>
<td>3.2</td>
<td>NXE1719</td>
<td>90°C</td>
<td>15/40/80</td>
<td>/</td>
<td>nBAa/IAAb</td>
</tr>
<tr>
<td>3.3</td>
<td>NXE1718</td>
<td>110°C</td>
<td>15/40/80</td>
<td>/</td>
<td>IAAb/nBAa</td>
</tr>
<tr>
<td></td>
<td>NXE1717</td>
<td>110°C</td>
<td>40</td>
<td>/</td>
<td>TMAHc</td>
</tr>
<tr>
<td></td>
<td>NXE1716</td>
<td>110°C</td>
<td>40</td>
<td>/</td>
<td>TMAHc</td>
</tr>
</tbody>
</table>

Table 1. Materials and processing conditions.

*a-n-Butyl Acetate, *b-Isoamyl Acetate, *c-0.026 N Tetramethylammonium Hydroxide

2.2. The dissolution rate monitor (DRM) tool

The tool is composed of four elements: the wafer/probe holder, the removable plate with five window cells, the developer supply and the measurement system, as seen in Fig. 1.

The wafer holder is suited for 300 mm wafer, allowing measurement after exposure on NXE3300 scanner. The removable plate can be screwed onto the holder and will contact the wafer only through the sealing rings of the cells. The developer supply is composed of an electronic syringe dispenser, delivering precise flow of developer (typically 50 ml/min) through pip ing to the cell, and finally to the waste drain.

The measurement system, by Ocean Optics, is composed of a tungsten halogen lamp (LS-1) light source, a Y-shaped optical fiber transmitter and receiver (the probe), and a USB2000+ spectrophotometer connected to a computer...
equipped with “SpectraSuite” software.

The light source emits blackbody spectra in the 300-1000 nm wavelength, with higher intensity in the 450-650 nm range, where we get two peaks of constructive interference with appropriate stack (photoresist coated on top of 1000 nm thermally grown silicon oxide), see Fig. 2, allowing measurement of resist thickness in the range of 0 to 100 nm.

Located in a class 1000 cleanroom environment, the room temperature is 22°C and the chemicals are used at this temperature during experiment.

2.3. Measurement procedure

On a 300 mm silicon wafer, a 1 µm thick silicon oxide layer is deposited at 400°C using PE-CVD tool PRODUCER (Applied Material). Actual thickness of this oxide layer is then measured by ellipsometry using KLA-Tencor SCD 100 ellipsometer.

Then, in a TEL Pro-Z track, photoresist is spin coated onto the substrate followed by PAB. Thickness of the photoresist film is measured on the same ellipsometer.

For experiment I and II, no exposure is performed and wafer are brought to the DRM tool.

In experiment 3, the wafer is exposed to EUV light using ASML full field scanner NXE3300: On the wafer, 5 fields are exposed at different exposure doses, directly followed by a post exposure bake. Thickness is again measured by ellipsometry to evaluate PEB resist shrinkage, and the wafer is brought into the dissolution rate monitor tool.

The coated wafer is then placed into the holder and the removable plate is meticulously screwed onto the holder to press the seals and avoid leakages. The holder is placed in a vertical position and connected to the developer supply and measurement system.

The actual measurement begins: spectra
collection is started simultaneously with the flow of developer, and data is collected typically every 10 ms (spectrum acquisition time) for 60 s.

Beforehand, on the DRM tool, a spectrum of a bare silicon wafer in a cell filled with developer solution has been collected as a reference spectrum.

The spectra obtained during measurement are then divided by the reference spectrum, in order to obtain the interference pattern of the oxide and the photoresist stack, effectively removing the contributions from the glass window and the wavelength-dependent intensity of the light source.

Using the measured film thicknesses and optical constants ($n$ and $k$) of the different layers of the stack, each spectra is converted into a photoresist film thickness, using dedicated Tokyo Electron Limited software “TEL Spectra Analyzer” to solve the interference equations [19] corresponding to the stack (Fig. 2). We consider $n$ and $k$ variation during dissolution [21] negligible.

The high sampling rate of spectrum collection provides the evolution of the thickness of the resist at a high temporal resolution, thus dynamically measuring the dissolution of the film when in contact with developer (see Fig. 3).

The curve of thickness through time is then linearly fitted to obtain the development rate (slope of the curve). This fit is realized on the linear part of the curve.

3. Results and discussion

The results of three experiments will be discussed: the first one is a validation of the tool and assessment of the performances. The second one present the impact of thickness variation on dissolution properties, and the utility of having very thin film measurement capabilities. The third one present the impact of quencher loading on dissolution properties in positive tone (PTD) chemically amplified resist (CAR).

3.1. Tool validation

In order to assess the tool precision, a repeatability test was realized. The tool is composed of five different cells spread over the horizontal diameter of the wafer. In Fig. 4, the dissolution rate measured under the same conditions on each cell is reported. The standard error on the linear fit for the development rate calculation is 1.5% and the 95% confidence interval for the development rate is [107.4 to 114.2], thus an average of 111 nm/s ± 3%, providing an estimate of the precision of the tool (sample-to-sample variation).

In order to frame the capability of our tool, we determined the minimum and maximum dissolution rate measurable.

The only limiting factor for a minimum dissolution rate measurement is the duration of the measurement. We consider that the limit of the tool is to detect a 1nm variation, and a realistic long measurement duration is 10min with the current set-up. Therefore, minimum rate is accurate down to 0.002 nm/s.

The maximum dissolution rate ($r_{lim}$) that can be measured by our tool is determined by

$$r_{lim} = \frac{L_{sample}}{t_{blackout} + n_{th} \cdot t_{aq}}$$

Where $L_{sample}$ is the photoresist film thickness, $t_{blackout}$ is the blackout time, $n_{th}$ is the threshold for the minimum number of measurement point needed for fitting (typically 10) and $t_{aq}$ is the acquisition time of the spectra collection.

As we want to measure EUV resist after exposure,
the thickness is usually below 50 nm, and for the high absorbance resist, thickness as low as 15 nm is usual.

To be able to measure fast-dissolving resist, we need to reduce $t_{\text{blackout}}$ and $t_{\text{aq}}$.

The novelty of this tool compared to similar tools described previously is the fact that the wafer, and thus the cell, is placed in a vertical position, allowing a uniform and fast (~2 cm/s) filling of the cell by the developer solution at the beginning of the measurement. The rapidity of this filling is important because at the moment at which the meniscus passes in front of the detector, it obstructs the measurement, leading to data loss (see Fig. 3 top). With our set-up, a $t_{\text{blackout}}$ of 50 ms was measured. This is half of what was reported with the horizontal set-up [10].

We also tested the influence of the scan capture rate ($t_{\text{aq}}$) on the measurement accuracy, varying acquisition time (10 ms – 5 ms – 3 ms – 2 ms – 1 ms). Results are reported in Fig. 4. The values obtained for the development rate at 1 and 2 ms are out of the 95% confidence interval of the actual development rate. But from 3 ms onwards, measurement accuracy is sufficient. The imprecision at fast acquisition time can be justified by the poorer fit quality due to a lower signal to noise ratio. $R^2$ value for the linear fit for 3 ms, 5 ms and 10 ms are above 0.99, but for 1 ms and 2 ms, they are at 0.93 and 0.97 respectively.

Maximum development rate for photoresist are typically between 100 and 500 nm/s. With a 3 ms $t_{\text{aq}}$ and a 50 ms $t_{\text{blackout}}$. We consider that dissolution rate up to 500 nm/s can be measured precisely with this tool for resist film of 40 nm. Equally, this means a 15 nm resist with faster dissolution rate than 200 nm/s will be totally dissolved during meniscus blackout.

3.2. Film thickness and developer impact

We have used the tool to assess the impact of resist thickness and developer solution on the dissolution properties.

Two negative tone systems where studied at different initial thicknesses: 80 nm, 40 nm and 15 nm. One system was dissolved with n-Butyl Acetate and the other with isoamyl acetate as developer solution.

In Fig. 3, we observe that in the case of the nBA, the dissolution rate is ~100 nm/s and is not strongly impacted by the thickness change.

But in the case of the second system, we observe two differences: At low thickness, the dissolution curve is linear with a rate of ~4.7 nm/s, but at higher thickness, the dissolution is not linear : we observe a slowing down of the instantaneous development rate with time, leading to a lower average dissolution rate for thicker resist.

![Fig. 4. Dissolution rate of Resist NXE1720 in nBA, for unexposed resist. Top, the measurement was repeated under similar condition in the five measurement cells of the set-up. Bottom, the acquisition time ($t_{\text{aq}}$) was varied for each measurement.](image)

Actually, if we look at the dissolution of the first 15 nm of resist for the 3 samples, they are very similar. But after this initial dissolution we observe important differences between samples.

In order to distinguish the effect of the photoresist from the effect of the developer solution used, we have developed each photoresist with both solvent. The dissolution curves obtained, presented in Fig. 5, show that in both case IAA induces a slower dissolution than nBA. This can be explained by the fact that IAA has a slightly higher molecular weight and is slightly more polar, and will thus less efficiently penetrate the hydrophobic photoresist film.

We also observe that NXE1719 dissolve linearly in IAA while NXE1718 shows a tail with nBA, which demonstrate that the non-linearity observed
in Fig. 3 is likely due to the photoresist composition and not due to the solvent.

Further, by comparing the two curves, we observe that the curve of NXE1716 is shifted towards higher dose, indicating that adding quencher in the resist formulation pushes the solubility switch to higher dose. This is consistent with the role of the quencher, used to increase resolution of the resist but at the cost of resist sensitivity.

These results brings up several conclusions: the tool is sensitive enough to detect variation in the dissolution behaviour of photoresist, even for resist film thickness as low as 15 nm; the development of a thin film of photoresist can be non-linear; In the case of non-linearity, the coating thickness can influence the development rate and behaviour.

This justifies the need for a DRM tool that can process photoresist samples at thicknesses relevant to the application, i.e. below 50 nm for EUV photoresists.

3.3. Quencher loading

As the tool developed can process 300 mm wafers, it is compatible with EUV exposure tools and allows easy data collection for dissolution contrast curves, i.e. the change in development rate as a function of exposure dose.

To assess the sensitivity of the DRM tool, we wanted to capture the impact of a slight change in resist composition onto the dissolution rate.

For this experiment, we have used two positive tone development resists that differ in composition only by their quencher loading. Resist NXE1716 has two times more quencher than resist NXE1717.

The dissolution rate as a function of exposure dose is reported in Fig. 6 on a loglog scale.

First of all, we observe a clear solubility switch (more than $10^4$ increase of the development rate) between exposed and unexposed resist for both resists.

Further, by comparing the two curves, we observe that the curve of NXE1716 is shifted towards higher dose, indicating that adding quencher in the resist formulation pushes the solubility switch to higher dose. This is consistent with the role of the quencher, used to increase resolution of the resist but at the cost of resist sensitivity.

We also observe that both $R_{\text{min}}$ (the minimum development rate, unexposed resist) and $R_{\text{max}}$ (the maximum development rate, fully exposed resist) for the high quencher resist are higher than for the lower quencher resist. This can be explained by a plasticizing effect of the quencher, that facilitate the solvent penetration in the polymer.

4. Conclusion

Multi-wavelength dissolution rate monitors are relevant tools for the study of development characteristics of thin EUV resist. The tool developed at imec provides accurate data collection at an acquisition rate as fast as 3 ms. The vertical flow of developer in the cell allows a fast air/liquid transition and permits to evaluate resists with fast dissolution (up to 500 nm/s).

This tool proved to be useful to capture differences in polymer dissolution properties for thin films: notably, film thickness and developer solution have an impact on the linearity of the dissolution.

The impact of quencher loading on dissolution was presented: the contrast curves obtained shows a clear shift of the switching dose, together with a plasticizing effect of the quencher.
Dissolution contrast curves of exposed EUV resists are measurable thanks to this tool and changes in the resist composition lead to significant changes in the dissolution properties.

This DRM tool provides an additional photoresist characterization technique to help resist manufacturer developing and testing new generation EUV photoresists, but also to collect inputs for computational lithographic software in their photoresist deprotection and patterning modelling.

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References