# Development Rate Monitoring (DRM)

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## 1. OBJECTIVE

The objective of this experiment is to understand and characterize the development and dissolution properties of photoresist materials.

## 2. INTRODUCTION

Development of conventional resist materials is based on image-wise dissolution discrimination. To understand and optimize photoresist development, it is necessary to characterize exposure dependent dissolution properties. The extraction of development rate and exposure relationships allows for tremendous insight into the imaging capabilities of a resist process. A family of normalized thickness verses development time curves for a resist material exposed at various dose levels can be generated. Such curves can be obtained using laser interferometry techniques and separate substrate exposure[1, 2] or a single substrate and multiple exposures[3]. A development rate vs. exposure curve can be produced from a family of these dissolution curves. To fully characterize the dissolution properties of a resist throughout its entire thickness, a rate curve may not suffice since development rate is a function of resist thickness. Surface inhibition reduces the development rate significantly at the top surface of the resist. Development rate vs. resist thickness curves show how development rate increases from the top surface of the resist toward the bottom.

When development rate and exposure are plotted in a log-log fashion, a linear region exists that can be described in terms of a development rate log-slope (DLS):

$$DLS = \frac{\partial \ln(dev.rate)}{\partial \ln(dose)}$$

Dissolution rate contrast can be expressed as:

$$Contrast = \frac{R_{max}}{R_{min}}$$

where $R_{min}$ and $R_{min}$ are the maximum and the minimum development rate respectively. Together, DLS and dissolution rate contrast are effective measurements of the dissolution properties of a resist material. High levels of both metrics are desirable. Furthermore, development rate can be related to exposure using models such as those developed by Mack[4]:

$$R(m) = \left[\frac{(a+1)(1-m)^n}{a+(1-m)^n}\right] R_{max} + R_{min}$$

where:

$$a = \frac{n+1}{n-1} \left(1 - M_{th}\right)^{n}$$

and $m$ is the relative concentration of the photoactive compound (PAC), $n$ is the selectivity, and $M_{th}$ is the threshold PAC concentration. Equation 14 and figure 7 in F. H. Dill's paper "Characterization of Positive Photoresist" can be used to either calculate or approximate the inhibitor concentration.

Control of the resist and development properties can be used to some extent to influence performance. A moderate contrast value near 10,000 is generally sufficient. As developer normality is changed, the $R_{MAX}$ and $R_{MIN}$ will both be affected (as long as base concentration does not fall below a critical level, pH ~12.5) but their ratio and the shape of the curve will remain fairly constant[5]. $R_{MAX}$ is primarily a function of the polymer itself. Major resist, sensitizer, and solvent factors that will influence development rate include:

- Polymeric structure
- PAC/PAG/inhibitor structure
- PAC/PAG/inhibitor concentrations (DNQ loading > 20%)
- Protection ratio (PHS protection ratio > 25%)
- Solvent concentration
- Polymeric molecular weight (>1.3 x104 g/mol)
- Polydispersity (< 3)
- Developer composition (metal ion vs. TMAH)
- Developer cation size and concentration
- Resist surfactant
- Resist dissolution inhibition/acceleration state
- Developer surfactant

Hydroxyl group positions on PHS polymer will also impact dissolution rate, a function of hydrogen bonding and steric hindrance with the polymer backbone[6]. Copolymers of 2- and 4-hydroxystyrene have been demonstrated to allow control of PHS dissolution properties.

## 3. PROCEDURE

This lab will involve the measurement of photoresist development rate.

### 3.1 Manual DRM procedure

1. Obtain several bare silicon wafer substrates (either 100mm or 150mm).
2. Either coat the wafers with photoresist by either hand or use the appropriate track (SVG or SSI).
    a. To hand coat, dehydrate bake the substrates at 100°C for 60 seconds and HMDS liquid prime at appropriate RPM, followed by a bake at 100°C for 60 seconds.
    b. Coat photoresist at appropriate RPM, and soft-bake at appropriate temperature for 60 seconds.
3. Measure thickness on the Nanospec at 5 radial locations on the wafer.

4. Expose the sample using either the GCA 6700 stepper with a blank reticle or the ASML i-line stepper.
    a. See section 3.2 for the stepper procedures.
5. Post-exposure bake the substrates at appropriate temperature for 60 seconds.
6. Pour approximately 250mL of MF CD-26 developer into a 9"x9" Pyrex dish. Monitor the temperature of the developer until it reaches room temperature. Using the 11-step time increment series [5, 5, 5, 10, 10, 20, 20, 30, 30, 30, 60, 60sec] insert the wafer into the developer for the time increment indicated then remove, rinse and measure (using the Nanospec) the photoresist thickness in the 16 die in the array for each step. An overall develop of 255 seconds will be used.
7. Plot:
    a. Photoresist thickness versus development rate for each exposure dose.
    b. From that plot generate a development rate versus exposure dose curve at 50% thickness
    c. And a ln(development rate) versus ln(exposure dose curve) at 50% thickness.
8. Calculate $R_{MIN}$, $R_{MAX}$, DLS, and Contrast.

## 3.2 Stepper procedures

### 3.2.1 GCA 6700 procedure

1. Make sure that the switch below the keyboard is in the "Time Mode" position.
2. Load the blank mask and first wafer.
3. EXPO EMCR221A
4. PASS: 1
5. STARTING ROW: 2
6. ENDING ROW: 9 (can be adjusted to lower number if necessary)
7. STARTING COLUMN: 2
8. ENDING COLUMN: 9 (can be adjusted to lower number if necessary)
9. OVER: E
10. Input the desired starting exposure time
11. Input the desired increment value
12. FOCUS: Use the most up-to-date focus setting (it should be written near the screen)
13. Do not run an open frame test
14. RETICLE BAR CODE: NONE (just hit "ENTER")
15. FLOOR #: enter the appropriate value.
16. ALIGNMENT MARK PHASE (P/N/X): X
17. Follow instructions in GCA user manual for wafer size being used.

### 3.2.2 ASML i-line procedure

Follow instructions in ASML user manual for Dose to Clear Test (Exposure Matrix).

## 4. Data Analysis

Plot the following from the data collected. The first few data points my need to be excluded if they were collected before the wafer was fully inserted (for the automated procedure). If standing waves are observed in the second plot, calculating an accurate slope may require averaging along a range.

1. A characteristic exposure curve (normalized thickness [$t/t_0$] versus log(exposure dose [mJ/cm$^2$])) for 30 seconds development time.
2. Normalized photoresist thickness versus development time [sec] for each exposure dose.
3. Development rate [nm/sec] versus relative exposure dose. Calculate development rate values at 50% normalized thickness, and normalize exposure dose to the dose-to-clear. This figure can be used to find $R_{MIN}$.
4. Development rate versus normalized photoresist thickness, for each exposure dose. Is surface inhibition observed? What causes this?
5. ln(development rate) versus ln(exposure dose). Calculate development rate values at 50% normalized thickness. Identify the linear region and calculate $R_{MIN}$, $R_{MAX}$, DLS, and Contrast.

Using the Mack model, fit $M_{th}$ and $n$ parameters to the data.

Explain any differences between the data collected from wafers that received a PEB and the data collected from wafers that did not.

## REFERENCES


1. K. L. Konnerth, F.H. Dill, IEEE Trans. Electron, Devices, ED-22, 453 (1975).
2. S. D. Chowdhury, D. Alexander, M. Goldman, A. Kukas, N. Farrar, C. Takemoto, B.W. Smith, Proc. SPIE 2438, 659 (1995).
3. For instance the Perkin Elmer Development Rate Monitor (DRM).
4. C. A. Mack, A Comprehensive Optical Lithography Model, SPIE 538, 207-220 (1985)
5. R. A. Arcus, Proc. SPIE 631, 124 (1986).
6. R. R. Dammel et al, Proc. SPIE 2195, 542 (1994).

## Manual DRM Data Sheet

(Use appropriate units)

| Develop Time | 5sec | 10 | 15 | 25 | 35 | 55 | 75 | 105 | 135 | 195 | 255 |
|---|---|---|---|---|---|---|---|---|---|---|---|
| **Exposure Dose** | **Remaining Resist Thickness (Å)** | | | | | | | | | | |
| 0 $mJ/cm^2$ | | | | | | | | | | | |
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