What is Lithography?

- The manufacture of an integrated circuit involves transferring a pattern to a substrate which ultimately has function.
- The term “lithography” is derived from lithos meaning “stone” and graphy to write” - literally “writing on stone”
- Our stone is a silicon wafer. We write using a photosensitive polymer called a “photoresist”.

Images courtesy of Chris Mack – lithoguru.com
The Lithographic Process

Printing at 130 nm, Intel can produce ~470 Pentium 4 chips from each 300 mm silicon wafer

Non-CA Polymer Resists

Current resist formulations typically use a PAG to increase sensitivity
- Chemical Amplification (CA)
Background - Moore’s “Law”

- Transistor density on integrated circuits doubles every couple of years.
- This exponential growth and ever-shrinking transistor size result in increased performance and decreased cost.
- What began as an observation has become a compass and engine, setting the bar for the semiconductor industry.

Source: www.intel.com

Industry Trends

- Reduction in wavelength with time
- Increase in NA with time
- 157 nm platform canceled due to cost and materials issues

\[ R = k \frac{\lambda}{NA} \quad \text{where } NA = n \sin \Theta_0 \]
Options being Explored

- Immersion lithography (193 nm)
- 193i+ (organic liquids)
- EUV lithography
- Non-CAR Resists
- Nanoimprint lithography (step and flash)
- Self assembly

Immersion Lithography

- A fluid is placed between photoresist and last lens element
  - Initially water (RI 1.43 @ 193nm)
  - Other high RI fluids being actively investigated by industry
- Makes possible lenses with >1 NA

\[ R = k_1 \frac{\lambda}{NA} \text{ where } NA = n \sin \Theta_0 \]
Importance of Refractive Index

- Increases NA
  - Allows smaller feature size
- Increase Exposure Latitude

Conley and Mack, Intl. Symp. Immersion and 157 nm Lithography Vancouver 2004

Current 193 nm Resist Polymers

- Solubility switch during exposure
- Adhesion
- $T_g$ modifier
- Etch resistance

Khojastch et al. (SPIE, 5039, 187 (2003))
Design Philosophy

- Include groups that increase refractive index
- Low Absorbance at 193 nm
- Low degree of interaction with water
- Posses properties of current resists
  - Adhesion, Etch resistance etc.

The QSPR Approach

Potential applications in the design of

Drugs
Catalysts
Polymers
Polymeric Composites
Solvents
Detergents
Pesticides, etc.
QSPR Modelling

Forward QSPR
Equations and algorithms which are capable of predicting molecular properties for a given structure.

Inverse QSPR
The molecular properties are the input; the output is the molecules which are calculated to satisfy the target properties.

Database Search
A database of known compounds is evaluated using Forward QSPR, and those most closely matching the desired properties are returned.


RI of Polymer vs. Repeat Unit

\[ R_{\text{polymer}} = R_{\text{unit}} + 0.09 \]

- Expect ca. 10-15% higher RI for polymers due to density increase
- Conclude we can use small molecules as models

\[ R_{\text{polymer}} = R_{\text{unit}} + 0.09 \]

Refractive index (polymer) vs. Refractive index (unit)
QSPR model at 589 nm

Five descriptors:

(+) Final heat of formation
(+) Molecular weight
(-) Relative number of H atoms
(+ ) Relative number of S atoms
(-) Number of F atoms

\[ RI = 1.07 \times 10^{-2} \times \frac{HF}{a\_count} + 5.4 \times 10^{-4} \times Weight \]
\[ -4.2 \times 10^{-1} \times \frac{a\_nH}{a\_count} + 4.7 \times 10^{-1} \times \frac{a\_nS}{a\_count} \]
\[ -2.6 \times 10^{-2} \times n\_nF + 1.66 \]

126 organic compounds

\( R = 0.96 \)

QSPR model at 193 nm

Five most significant descriptors:

(-) HOMO-LUMO energy gap
(-) Number of Cl atoms
(-) Relative number of Br atoms
(+ ) Number of S atoms
(+ ) Number of F atoms

Other significant descriptors:

(-) Relative number of benzene rings
(+ ) Relative number of carbon atoms

64 organic compounds

\( R = 0.87 \)
Database Screening

- Generate a database consisting of compounds of interest
- Enter these into QSPR Models
- Obtain list of candidates with high RI
- Refine based on synthetic restrictions

Example Targets

T1   T2   T3   T4   T5

Predicted $n_{193}$

1.70  1.69  1.68  1.71  1.62

Experimental $n_{193}$

1.96  1.90  1.88  1.90  1.81
Monomer Synthesis

Starting materials

+ Methacryloyl chloride

Corresponding methacrylamide, thiomethacrylate or methacrylate

RI of Homopolymers

- Prepared by free radical polymerisation

<table>
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<tr>
<th></th>
<th>P1</th>
<th>P2</th>
<th>P3</th>
<th>P4</th>
<th>P5</th>
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<tr>
<td>Predicted $n_{193}$</td>
<td>1.96</td>
<td>1.90</td>
<td>1.88</td>
<td>1.9</td>
<td>1.81</td>
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<tr>
<td>Experimental $n_{193}$</td>
<td>n/a</td>
<td>n/a</td>
<td>2.01</td>
<td>1.98</td>
<td>1.92</td>
</tr>
</tbody>
</table>
Resist Polymer Synthesis

- Two synthetic routes chosen:
  - Copolymers of MAdMA* with:

```
+       N=N
M1      N=N
+       N=N
M2      N=N
+       N=N
M3      N=N
+       N=N
M4      N=N
+       N=N
M5
```

- Flexible routes to main-chain heteroatoms

Example Structures

- All polymers formulated ~6 wt% solids in PGMEA or cyclohexanone
- 5 wt% PAG TPS-nF
- 0.3 wt% Base TBAH
Results - Polymer CP1

CP1

- $R_l_{193nm} = 1.7025$
- $Abs_{193nm} = 5.216/\mu m$
- $T_g = 106 \, ^\circ C$
- $M_w = 10.8 \, k$
- $E_o \sim 25 \, mJ/cm^2$

What is happening?
- Slow
- Thiadiazole too basic?
- Low Tg
- Methyl group?

Results - Polymer CP2

CP2

- $R_l_{193nm} = 1.7630$
- $Abs_{193nm} = 5.216/\mu m$
- $T_g = 166 \, ^\circ C$
- $M_w = 68 \, k$
- $E_o \sim 5.5 \, mJ/cm^2$

What is happening?
- Clears
- MW too high
- Chain transfer agent
- $T_g$ marginally high
- Terpolymer
Results – Polymer CP3

CP3

- $R_I^{193\text{nm}} = 1.804$
- $A_{b s}^{193\text{nm}} = 7.228/\mu\text{m}$
- $T_g = 140 \, ^\circ\text{C}$
- $M_w = 5 \, k$
- $E_o \cong 3 \, \text{mJ/cm}^2$

Not imaged - this polymer was found to interact with the top coat

Exposure conditions
- $\text{PAB}=120, 60\text{sec}$;
- $\text{PEB} =130, 60\text{sec}$;
- $\sigma = 0.7$
- Immersion fluid : Water

Imaging Results

CP2

- $R_I^{193\text{nm}} = 1.7630$
- $A_{b s}^{193\text{nm}} = 5.216/\mu\text{m}$
- $T_g = 166 \, ^\circ\text{C}$
- $M_w = 68 \, k$
- $E_o \sim 5.5 \, \text{mJ/cm}^2$

Exposure conditions
- $\text{PAB}=120, 60\text{sec}$;
- $\text{PEB} =130, 60\text{sec}$;
- $\sigma = 0.7$
- Immersion fluid : Water
Effect of Sulfur on Absorbance

\[ \%S = 14.69\% \]
\[ R_{193\text{nm}} = 1.762, \quad 0.0042/\%S \]
\[ \text{Abs}_{193\text{nm}} = 5.212/\mu\text{m}, \quad 0.35/\mu\text{m} \%S \]
\[ E_0 = 6\text{mJ/cm}^2 \]

Effect of Sulfur on Absorbance

\[ \%S = 25.34\% \]
\[ R_{193\text{nm}} = 1.804, \quad 0.0041/\%S \]
\[ \text{Abs}_{193\text{nm}} = 7.23/\mu\text{m}, \quad 0.28/\mu\text{m} \%S \]
\[ E_0 = 3\text{mJ/cm}^2 \]
Effect of Sulfur on Absorbance

\[\%S = 23.5\%\]
\[RI_{193\text{nm}} = 1.824, \ 0.0052/\%S\]
\[Abs_{193\text{nm}} = 10.74/\mu m, \ 0.46/\mu m \%S\]
\[E_o = 22\text{mJ/cm}^2\]

Effect of Sulfur on Absorbance

\[\%S = 36.12\%\]
\[RI_{193\text{nm}} = 1.904, \ 0.0056/\%S\]
\[Abs_{193\text{nm}} = 13.75/\mu m, \ 0.38/\mu m \%S\]
\[E_o = 12\text{mJ/cm}^2\]
Resist Limits to Lithography

Resolution
- Absorbance of the resist
  - Fewer photos reaching PAG

Effect of resist absorbance on resist profile

Absorbance = 0.6/μm
Absorbance = 2/μm
Absorbance = 4/μm

Limits on Sulfur Content

- Difficult to control position of absorption maximum, although models are available
- Assuming maximum acceptable absorbance = 4/μm then:
  - Can incorporate 9-14 wt. % S
  - Thioester/Thiazoline gives highest Abs/μm
  - Thioether/sulfone gives best trade-off, i.e. best RI/Abs193 nm
  - Using this approach n\(_{w1}(max)\) ~ 1.8-1.85
Alternative Structures

Methacrylate polymer ligands being prepared by LRP
- Control of MW and MWD
- Functional chain ends

Conclusions - Part 1

- Design rules have been refined
  - Maximum sulfur levels for incorporation into resists have been defined

- Difficult to get above 1.8 - 1.85 and to achieve a working resist polymer

- Two new platforms being investigated

- Metal oxide nanoparticles
Some Resist Challenges

- Many challenges in the development of EUV technology
  - Resist Development currently rated #1 (EUVL 2006)

LINE-EDGE ROUGHNESS
3σ < 1.5 nm

SENSITIVITY
5 mJ cm⁻²

RESOLUTION
< 32 nm

Resolution

Resist Limits to Lithography

Resolution
• Acid diffusion
  • Blurring of image features

Effect of acid diffusion on resist profile

Diffusive pathlength = 70 nm  Diffusive pathlength = 120 nm  Diffusive pathlength = 150 nm

Prolith Program, KLA-Tencor
Extreme Ultraviolet Lithography

- Emerging technology
- 13.4 nm / 92 eV photons
- Xe or Sn plasma source

Why EUV?

• Want to write increasingly small features
• Decreasing λ increases resolution
  For 13.4 nm can get R < 32 nm \( R = k_1 \frac{\lambda}{NA} \)

Rational Design Approach

• Determine if a knowledge of the γ radiation sensitivity of polymers can be used to aid in the design of EUV resists and to screen candidate materials
• High-throughput measurement of the sensitivity to degradation of model compounds as input for the QSPR model
• The development of a Quantitative Structure-Property Relationship (QSPR) to guide the synthesis of high sensitivity polymer resists
• Synthesis of high sensitivity positive tone resists
Correlation between EUV and $\gamma$

Hypothesis

- 1 MeV irradiation model will be a good predictor of performance at 92 eV
  - Predominantly Low-Energy Secondary Electrons ($< 70$ eV) that result in degradation

Experimental

- Compare yield of scission products $G(s)$ at both energies
- $\gamma$ Irradiation using $^{60}$Co source at UQ (ca. 2.5 kGy hr$^{-1}$)
  - Bulk polymer, $10^{-3}$ mTorr and at ambient T
- EUV irradiations carried out at U @ Albany, NY
  - $\sim$ 50 nm films spin coated onto silicon wafers, $10^{-6}$ mTorr

Methodology

- Samples dissolved in THF and $M_n$ measured by GPC
- $G(s)$ determined from $M_n$ as a function of dose

\[
\frac{1}{M_n(D)} = \frac{1}{M_n(0)} + 2k_1G(S)D
\]

- For $\gamma$ irradiations $D$ is determined by Fricke dosimetry
- For EUV dose values are less defined as the LET values difficult to calculate at 92 eV:
  - Measure incident energy and assume that all of the energy adsorbed is converted into KE
  - this probably overestimates the true dose
Radiolysis of PMMA

\[ \gamma - 1\text{MeV} \]
\[ G(s) = 1.2 \]

\[ \text{EUV} - 92\text{ eV} \]
\[ G(s) = 0.4 \]

Radiolysis of PIB

\[ \gamma - 1\text{MeV} \]
\[ G(s) = 2.3 \]

\[ \text{EUV} - 92\text{ eV} \]
\[ G(s) = 0.7 \]
**Comparison $\gamma$ - EUV**

![Graph showing comparison of $\gamma$ - EUV]

**Second QSPR Model of Sensitivity**

70 eV Input Data

Stability Index - SI

- Proposed to be a measure of stability to ionization

Measure stability by GC-MS

- MS-Electron Ionization – 70 eV ~ 17.6 nm
- Fast throughput (100+ samples measured)
70 eV (Mass Spec) Model

- Use electron ionization source of a GC-MS
  - MS-Electron Ionization – 70 eV ~ 17.6 nm
  - EUV Source at Albany – 11 – 17 nm

QSPR Model of Sensitivity

Initial model uses 5 descriptors
- 3 are related to charge
- HOMO energy
- C-H bond energy

Further work is still required to separate high sensitivity materials

- Model is used to guide in the choice of structures to be targeted
- Can also use it to predict the relative sensitivity of novel materials
QSPR Model of Glass Transition

- Uses 271 polymer $T_g$ from literature
- Assumes high MW
- Good correlation with 4 descriptors
- Can be used to predict $T_g$ of copolymers also

Examples

Predicted $T_g$:
- 43 °C
- 74 °C
- 132 °C

Incorporation with high sensitivity target materials => Predicted $T_g$ for target materials

Some Initial Materials

Material I – Copolymer of predicted target functionality

- See increase in G(s) with increasing target function concentration
- G(s) values increase by factor of 3
- Homopolymer is currently difficult to prepare by conventional methods
Second Generation Materials

Material II

<table>
<thead>
<tr>
<th>Dose (kGy)</th>
<th>1/Mn (mol kg⁻¹)</th>
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</table>

Initial Homopolymer
Sensitivity – G(s) ~ 8
Low glass transition and poor MW control

Modified Copolymer
Sensitivity – G(s) ~ 1.3
High Glass transition (~ 120 ºC) with Good MW Control

We are currently developing synthetic routes for preparing a range of these copolymers

Conclusions Part 2

- QSPR models for sensitivity and T_g have been developed
  Use a combination of high throughput screening and literature
  Use models to predict structural classes to target

- Synthesis of target materials
  - Have developed synthetic pathways that allow control of MW and physical properties
  - Initial screening for sensitivity by γ irradiation is promising