“Sufficiently large objects must necessarily contain a given structure. Complete disorder is impossible.”

Ramsey theory-
A branch of mathematics that studies the conditions under which order must appear.

Interfacial Dynamic Mesoscopic Structuring - a Highly Probable Origin of the Mysterious LER “Fundamental Limit”

Yehiel Gotkis
Even Classic Homogeneous Solutions Like Methanol and Water Undergo Segregation

- At high concentrations—~ 1:1 molar—methanol and water are considerably more involved than appears to be the case at first sight. Molecular Segregation Observed in Concentrated Alcohol-Water Solution by Dixit et al., Nature, 416, 829-832 (2002)
- The concentrated mixture only appears to be homogeneous, and on a molecular scale the mixing is incomplete, showing segregation of H-bonded strings and clusters
- Ideal dissolution behavior occurs only at < 0.1 molar concentrations.

“So, it matters now mucn water you add to your scotch”
Keith Standiford....
Moor’s Law, Being a Scaling Law, Requires…
At the Moment the Litho LER Refuses to Scale Down, as Dr. G. Moore Prescribed…

193i Technology (45nm Half Pitch)

Addressed in part by ISMT
Addressed by others
- Potential Showstopper / Requires Invention
- Critical Issue / Development Required
- Solution Known
Long-λ Waviness Generates Most of the LER

To resolve the LER issue the origin of the long-range ($10^2$-$10^3$ nm) LER features must be understood!

\[ \zeta = 40 - 500 \text{ nm} \]
Material Structures of $10^2$ - $10^3$ nm Scale Are Known As Mesoscopic Structures
Considering LER, Together With Shot Noise, Acid Diffusion, Polymer Size, etc…

We should be also concerned about

**Thin Film Mesoscopic Structuring**

Three phenomena most likely inducing MS and associated LER contribution will be discussed in this presentation:

- **Marangoni-Bernard instability** in liquid films due to thermal gradients and solvent evaporation *(Spin, SB(?))*
- **Stress-induced interfacial structuring** due to sharp differences in properties of protected and deprotected sections *(PEB)*
- **Thermo-chemical patterning** at the dissolution interface *(Develop)*
Lithography, Ultimately, Is a Sequence of Chemical Transformations...

Chemical rates are sensitive to any variation within the system: of structure, composition, density, impurities, by-products, agitation, temperature; actually everything is capable of introducing chemical non-uniformities.

... and Chemistry is a very sensitive lady sensing even very fine structure/composition variations.
If Resist Thin Film Is (MS) Structured …

Catalytic transformation (Deprotection) and polymer dissolution (Development) rates certainly will be modulated according to the film structural network.
So...

Is there any Physics/Chemistry capable of inducing structural units, consistent with $10^2 - 10^3$ nm long-range LER component in TFs?
Interfacial Phenomena: Strong Interfacial Effects Make UTRFs to Be a Completely New Entity to Deal With.

UTFs: No bulk volume.

With no bulk...

- UTFs become highly interfacial with interfacial phenomena dictating the rules of the game.
- UTFs lose the most fundamental material attribute—constancy of basic properties (MP, BP, Density, T/D parameters, etc.), which become strongly dependent on film thickness, substrate(s) nature, surface state and so on.
- UTF properties become also strongly influenced by interfacial instabilities, which significantly affects the UTF processing responses.
- Even conventional theories, developed in terms of properties as constants, may require significant amendments for UTFs.

Interfacial effects turn out to be the dominant factors for UTFs, influencing all their responses, thermal, chemical, optical, mechanical, dynamic, etc.
Marangoni-Bernard Instability

I. RTF is a highly evaporating liquid film during spin step

Convection disturbs all sub-systems around, causing:
- unstable geometry
- thermal non-uniformity
- compositional non-uniformity
- chemical activity and phase transitions at the upper and lower interfaces
Marangoni-Bernard instability structures the resist films
Dynamic Liquid Structures Are Transferred Into Solidified Films

- LTFs are
  - never static
  - never flat
  - never uniform, neither thermally nor chemically or structurally.

Once the LTF is solidified, dynamic NUs are turned into structural NUs patterning film properties and its chemical activity.

How “good” is good?
Even Atomic Non-Evaporating Liquid UTFs Develop Instabilities

As per

\[
M = \frac{\Delta T h}{\rho \nu k}
\]

convections

should not develop for UTFs.

However

Here it is molten 100 nm PVD Cu film, highly thermoconductive, no evaporation

And it swiftly develops intense instability!

(though being just 100 nm thick it should not!!!)
Stress Accumulation as a Cause for Interfacial Re-structuring at the Chemical Front During PEB

II. Mechanical & Thermal stress induced instability at the Protected/Deprotected interface (PEB)

The deprotected section wants to shrink, causing stress accumulation.

Combined thermal and mechanical stress together with elevated temperature $T \sim T_g$ induce instability.

<table>
<thead>
<tr>
<th>IM bonding</th>
<th>$R_P$</th>
<th>$R_D$</th>
</tr>
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<tbody>
<tr>
<td>Weak</td>
<td>Strong/H</td>
<td>High/Compress</td>
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<tr>
<td>Low</td>
<td>High</td>
<td>Hard</td>
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<td>Low</td>
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<td>Soft</td>
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$T_{MP}$ ($T_g$) Density Stress Hardness
While Processing, We Frequently Bring Our Stressed Resist Films Close to $T_g$ ...

...providing the film significantly increasing the system mobility with its structure what it wants to do ($T -< MP$) (and not we would like)
Develop Step Is Associated With Another Patterning Phenomenon

Upper phase: 0.25 mol/l propionic acid in cyclohexane; lower phase: TMAH in water

III. Thermo-solutal instability at chemically active interface (DEVELOP)

Time-dependent (@0.25 mol/l TMAH)

Strong intrusions into acidic media develop already in 1.6 min

Concentration (TMAH)-dependent (@t=35 min)

0.063 mol/l 0.125 mol/l 0.25 mol/l 0.5 mol/l 0.75 mol/l

5.75 min 14.1 min 22.8 min 41.1 min 1.6 min

Super-acids in CARs
MS During Develop May Cause Feature Shape/Size Dependent LER/LWR Effects

“SEM of partially developed line...”

How Can We Learn About the MS?

Two general approaches could be proposed to reveal the MS:

- Introduce contrasting materials, density of which will be re-distributed by the MS mechanism.

- **Use sequential ChemDiss (partial develop).**
  - To avoid interference with exposure&CAR shot noise do it in a non-patterned Z-dissolution mode.
  - Investigate surface profile RMS and PSD at the Z-dissolution front.
Z- Dissolution Dynamics:  
I. RMS Analysis

- Let us assume that
  - The most stable structural units, are the most abundant, occupying the most of material volume.
  - The more stable the unit the lower its z-dissolution rate.

- Then during dissolution
  - The RMS initially increase
  - The more abundant and stable units accumulate over the surface, jamming the dissolution.
  - The RMS\textsubscript{max} stays at its max value until the bottleneck is breached.
  - When the tallest slow sections are breached, the laying beneath quickly dissolving units catch up.
  - The RMS goes down and then again rises back.

- This results in RMS oscillations if the structures within the scanning area are not distributed perfectly random, (skin, layers, interfacials etc.)

- Comparison of different samples at the same dissolution depth may lead to incorrect conclusions

- Oscillation λ-s carry information about the system structural content

- If some other type of Z-structuring exists, it may interfere and mask the intrinsic structural effects

- Self-created (or externally induced) dissolution inhibiting layers cause RMS oscillations.
Z- Dissolution Dynamics:
II. FFT 2D PSD- Another Very Powerful Instrument

... to probe the MS content at different TF depths as function of process state and conditions

- The more film THK is dissolved the more pronounced becomes the film structural content (or Dissolution rate MS-modulation)
- Even the polymer only film (w/no PAG) showed high content of 50-1000 nm structures (MS), responsible for the dominant part of RMS.

Note: The images and graphs are for explanation purposes not representing the actual data.
There is absolutely no reason to hope that resist film processing will proceed without rate modulation!

There are at least 3 phenomena, likely to induce dynamic MS effects and associated long-\(\lambda\) waviness:

- **Marangoni-Bernard instability in liquid resist films** due to solvent evaporation (Spin)
- **Stress-induced interfacial structuring** at the line edge due to differences in properties of protected and deprotected polymers and \(T \sim T_g\) (PEB)
- **Thermo-chemical patterning at the dissolution interface** due to chemical activity (Develop)

Being not sensitive to conventional shot noise parameters, these contributions appear as "LER fundamental limit".

Being comparable or prevailing over CAR effects and thus masking them, the MS effects strongly complicate progress in LER improvement.

Ways to deal with all this stuff:

1. **Invent LER repair (smoothing) technology** (like post-Develop rinse, or...), although it is very hard to believe the long-\(\lambda\) waviness with \(\lambda \gg \text{amplitude}\) could be straightened

2. **Identify, suppress or anneal** MS developments at all steps of the litho sequence.
Acknowledgements

- Leonid Baranov  - fruitful discussions and FFT-2D package
- Keith Standiford  - fruitful discussions and very bright ideas

Thank you for your attention!
Back-ups
One may say: “The data is scattered and mostly not directly related to the resists…”

Well, in many cases it is not really necessary to see the overall picture, to identify the matter, just only the tip of the tail.
Bottom Interface Adds Its Strong Signature to the UTF Structure

Substrate differences (chemical origin, solute and solvent interfacial molecular arrangement and interfacial interaction, surface roughness, charge, defect density etc.) induce differences in film solidification dynamics and its final structure.