Understanding photoresist - electroplating bath interactions using HPLC methodology

I. Popova*, R. Dieckmann*, N. Schroeder*,

G. Gomes**, J. Golden**

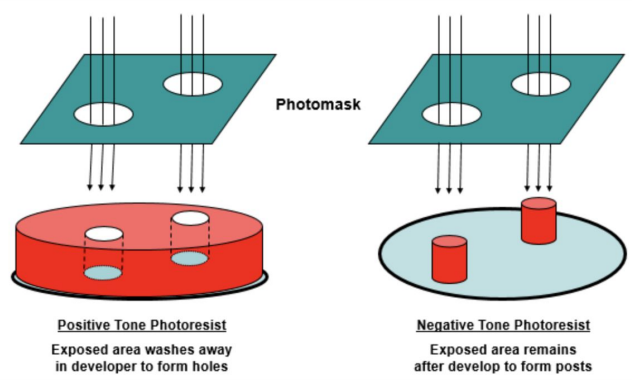
*ancosys Inc, 100 Cooperative Way, Kalispell, MT 59901, USA

**KemLab, 254 W. Cummings Park, Woburn, MA 01801, USA

Problem statement - Photoresist detection

- During plating process – especially at extended plating times resist components are leaching into the bath
- New packaging solutions require **new resist materials and new baths,** due to both new design rules and stack materials
- Resist misprocessing – under-bake, coating issues (ie film pinholes and delamination) contribute to contamination
- **This study is an attempt to simulate effects of full wafer plating in bath material, using model experiments**
- How can we reliably detect signs of photoresist leaching ?
- Do photoresist impurities in electroplating Cu baths affect the plating process?
- Can different photoresist types be compared with each other?
- Can a simple and general procedure for characterization be set up?
- Can this understanding lead to designing better packaging resist materials ?

Photoresist processing



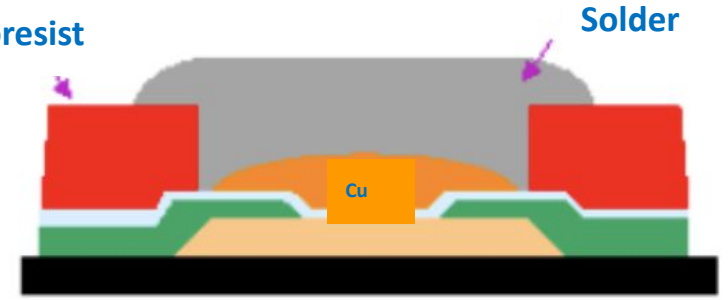
- Modern negative and positive PRs offer same capabilities and differ largely in material design only

- Both types are used broadly alongside polyimide (PI) materials in packaging

https://imicromaterials.com/technical/lithography-process-overview

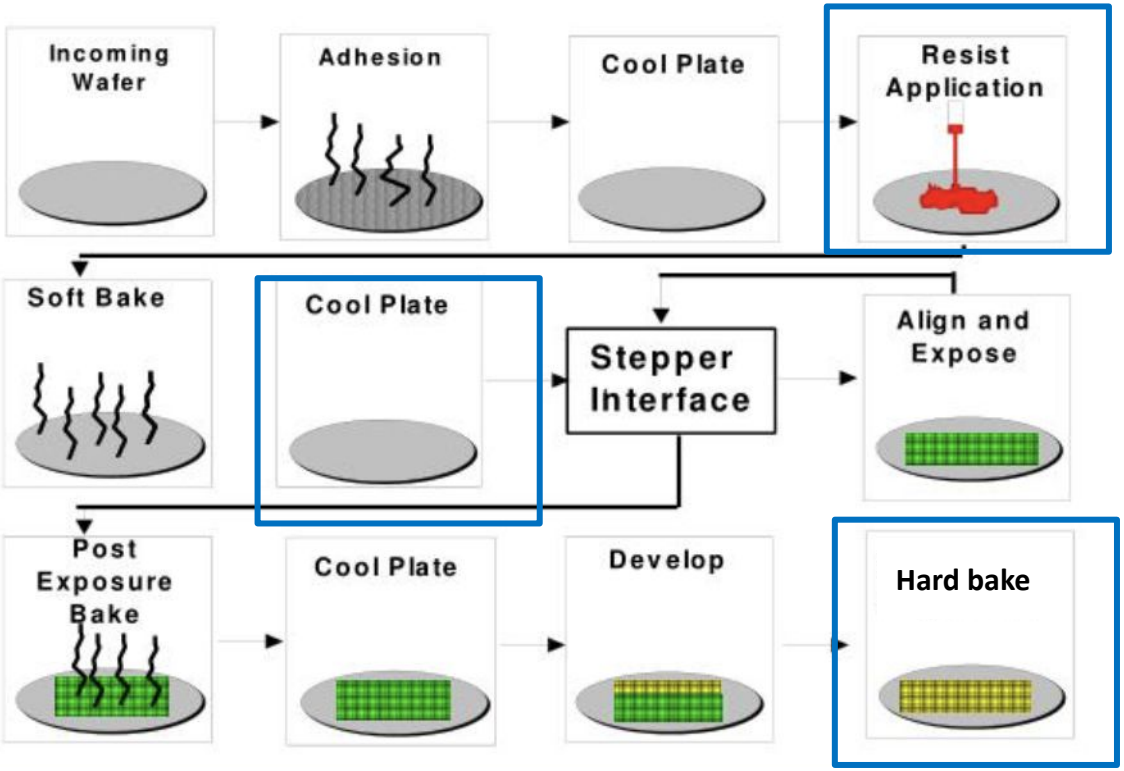
- Stability of PR film is tested several times when a metal stack for bump or an RDL is defined in packaging process flow

- Under plating bath attack PR film may swell, leaching components and may worse case delaminate



Nordic Electronics Packaging Guideline

Photoresist processing

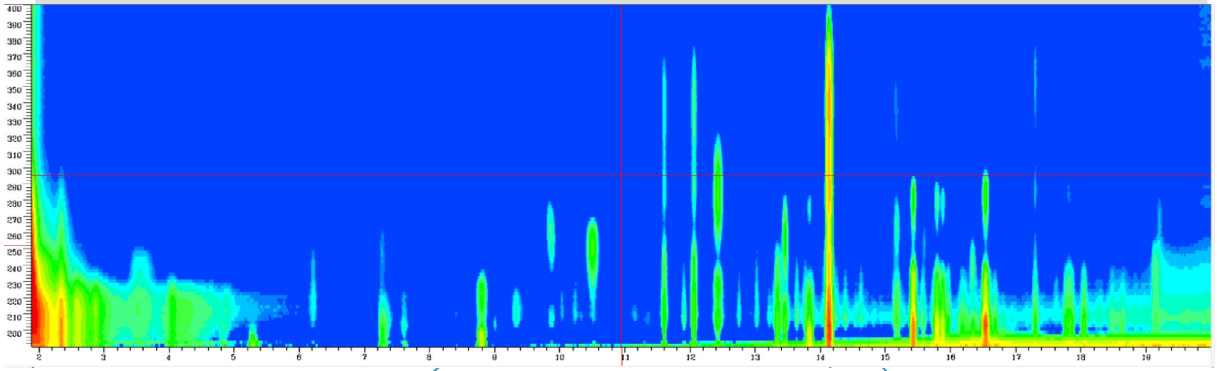


PR detection - benefits of complex approach

Detection method	Conc vs responce	Sensitivity	Specificity	Complications
HPLC	Direct detection	High / but small signal	High	• Need to deconvolute resist signal to improve S/N and detection limits • Detects only PR fragments and UV-active compounds
EC methods	Indirect - effect on plating	Low / signal strong	Low	Signature may overlap with other effects
Surface Tension	Direct detection	High	Easy to operate with no extra chemicals	Limited to surface-active components

Complexities of HPLC Investigation

HPLC Measurement of bath with organic additives



Additional Peaks

Change in Shape or Quantity of the Additive Peaks

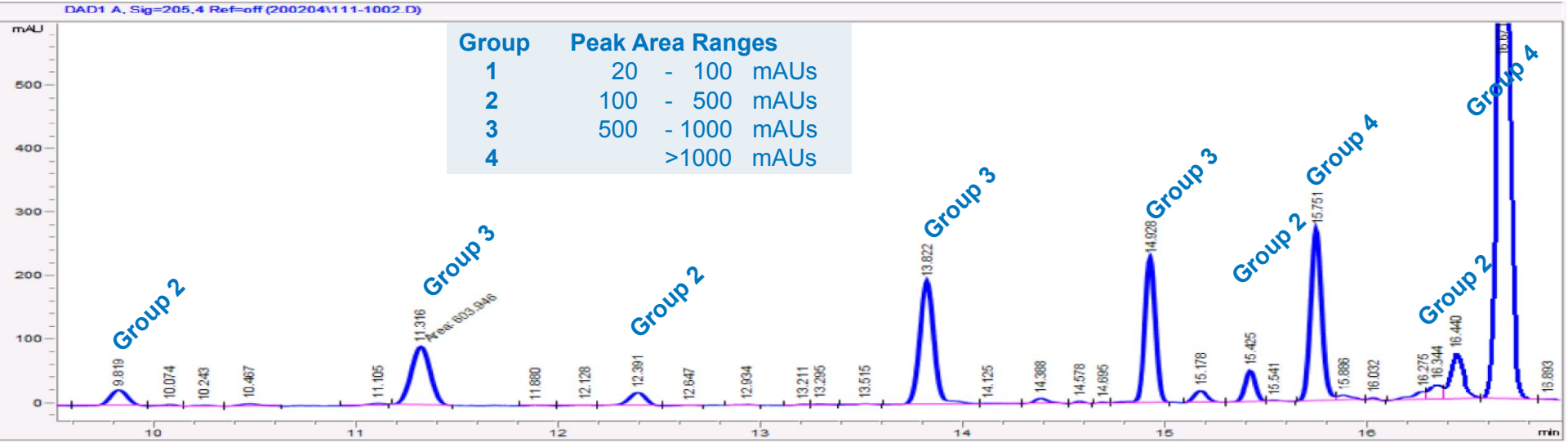
Photoresist (PR)

Breakdowns (BD)

Caused by Plating Process

Influenced by PR

Leaching Photoresist – Methodology



Group	Peak Area Ranges
1	20 - 100 mAUs
2	100 - 500 mAUs
3	500 - 1000 mAUs
4	>1000 mAUs

- Peaks considered if they appear from contact with PRs.
- For a simplified comparative illustration of the measured PR related peaks Groups and Classifier were generated.

➢ **Group** corresponds to Peak area classification at given retention time

➢ **Classifier** means counts multiplied by group (e.g. 4 x Group 2 + 3 x Group 3 + 2 x Group 4 = 25)

Aim of the approach:

Fingerprint picture instead of total quantification

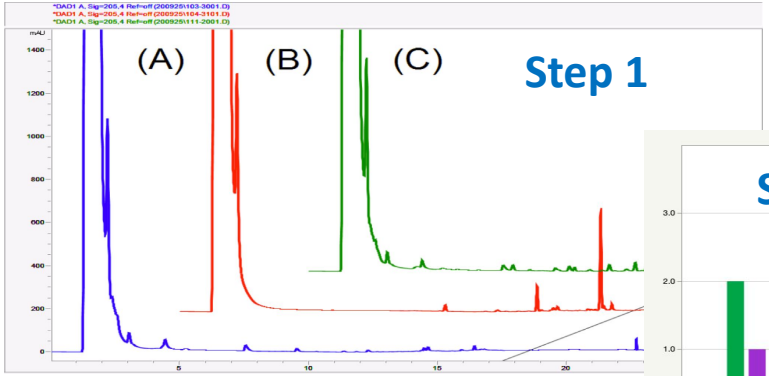
Leaching Photoresist – Resist materials used

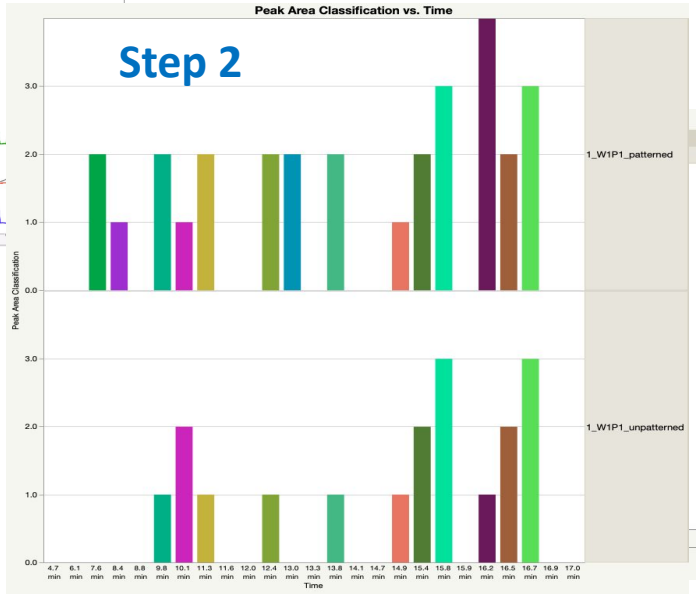
Wafer	PR Name	Comment
W1P1	K-Pro15 Pos,Tone	Packaging resist (for plating – higher Mw) unpatterned wafer
W2P2	competitor Pos. Tone	Packaging resist (for plating -higher Mw) unpatterned wafer
W3P3	KL6008 Pos,Tone	general-purpose; standard Mw) unpatterned wafer
W1P1 (pat.)	K-Pro15	Packaging resist (for plating)
W2P2 (pat.)	competitor	Packaging resist (for plating)
W3P3 (pat.)	KL6008	general-purpose
W4P3 (pat.)	KL6008 Pos.Tone	general-purpose, lower soft bake

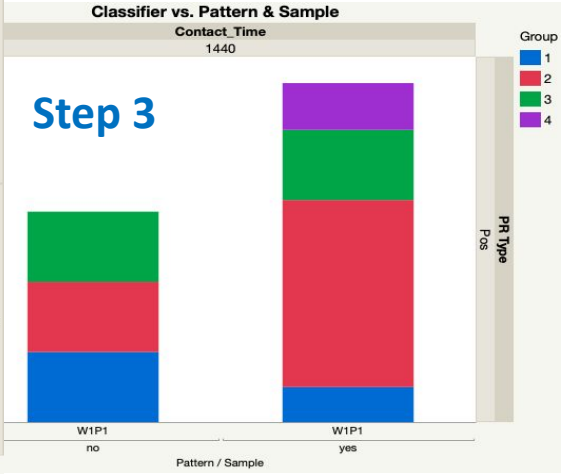
Wafer	PR Name	Comment
W4N1 - NegTone	competitor	unpatterned wafer
W9N1 -Neg.Tone	competitor	patterned wafer
W5N2-Neg. Tone	APOL-LO 3207	unpatterned wafer
W8N2-Neg. Tone	APOL-LO 3207	patterned wafer

- To make sure findings can be generalised - several resist materials both from KemLab and leading material manufacturers were compared
- Dow8540 copper plating bath material was used in the study, as a representative

Methodology - Bath Composition







- **Raw Chromatograms:**

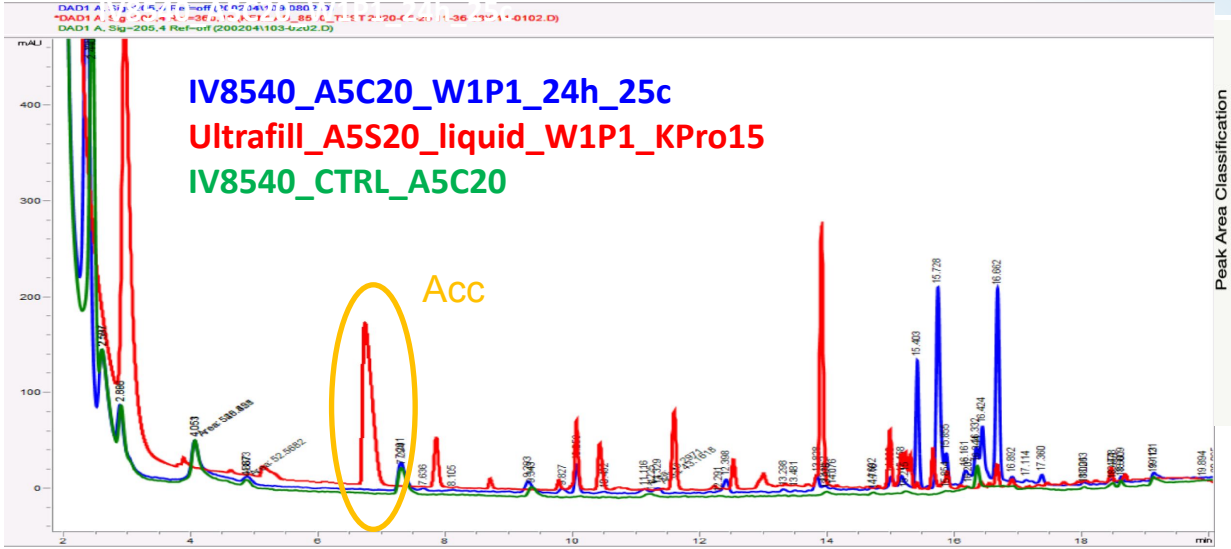
(A) Reference without contact to photoresist;
(B) VMS on W1P1 (patterned) wafer for 1 day;
(C) Full bath solution on W1P1 (patterned) wafer for 1 day

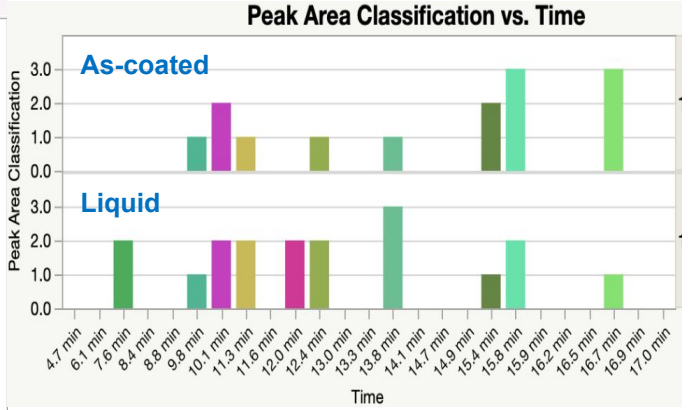
- **Classification of the peak area in groups:** Schematic representation of the chromatograms unpatterned wafer - below; patterned - above

- **Classifier for comparison of different wafers:**

W1P1 unpatterned - left bar; W1P1 patterned - right bar

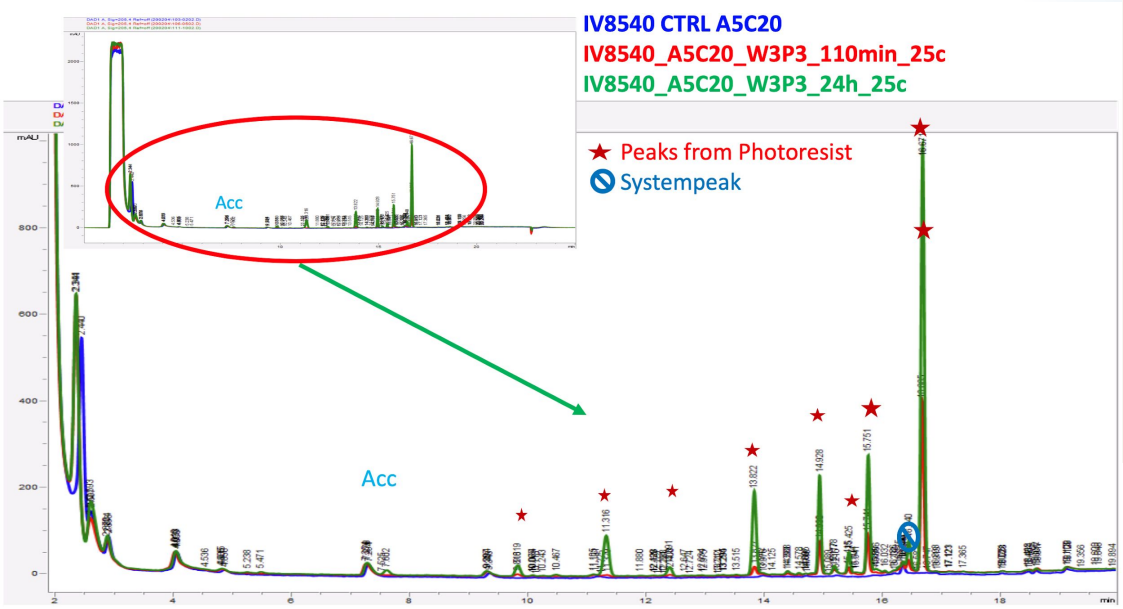
Leaching Photoresist - Sample preparation

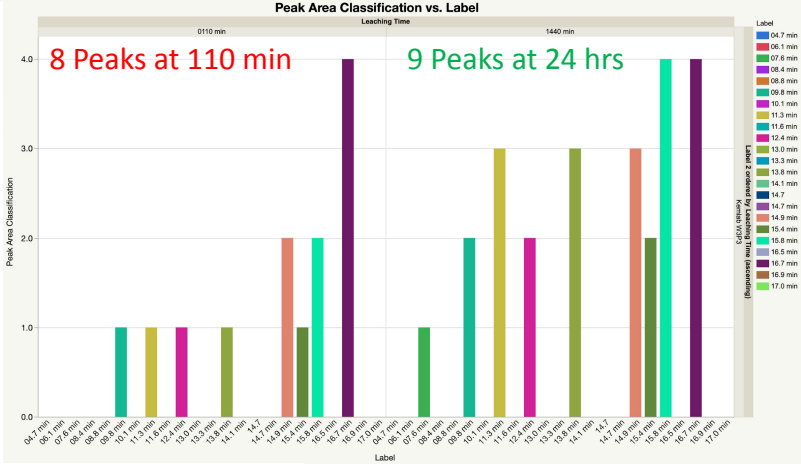




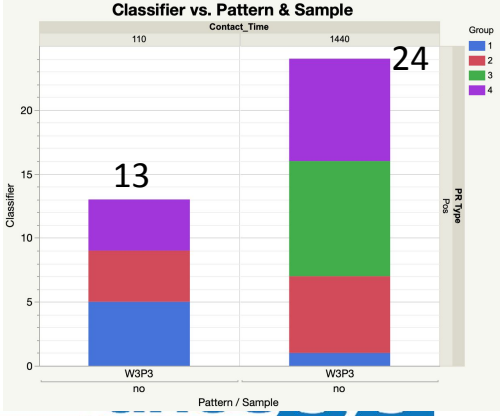
- Relative difficulty of accessing patterned full stack wafers makes it hard to create resist / stack specific PR signatures
- Using developed here methodology signature of the PR leaching can be created even using a relatively easier to obtain liquid resist sample

Leaching Photoresist - Contact time for general purpose PR



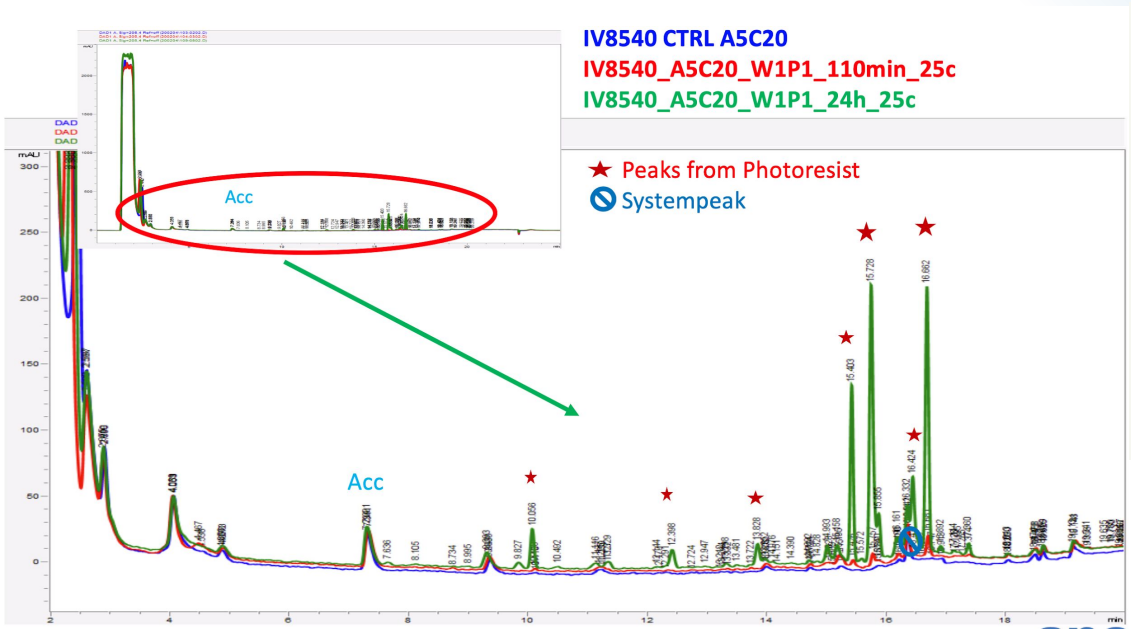


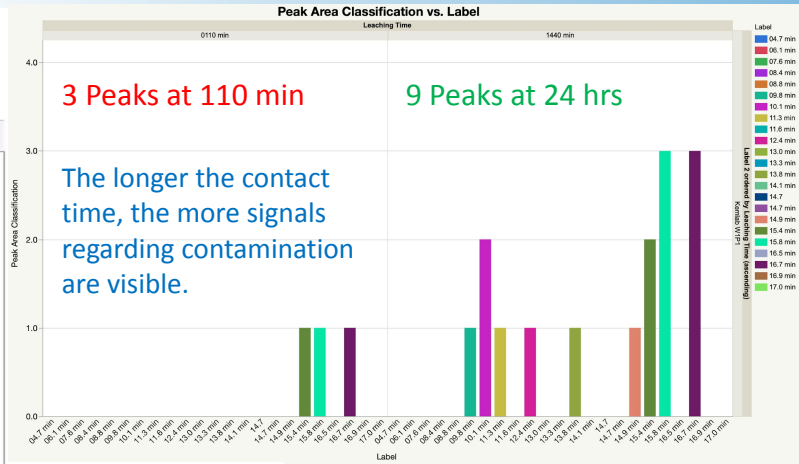
W3P3



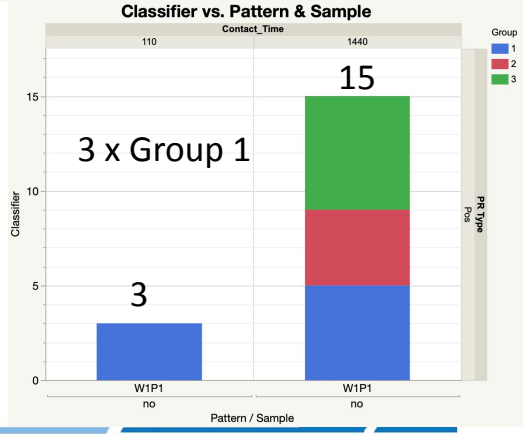
- With longer the contact time, intensities of the seen peaks are increasing. Peak numbers are relatively unchanged.

Leaching Photoresist - Contact time for packaging PR





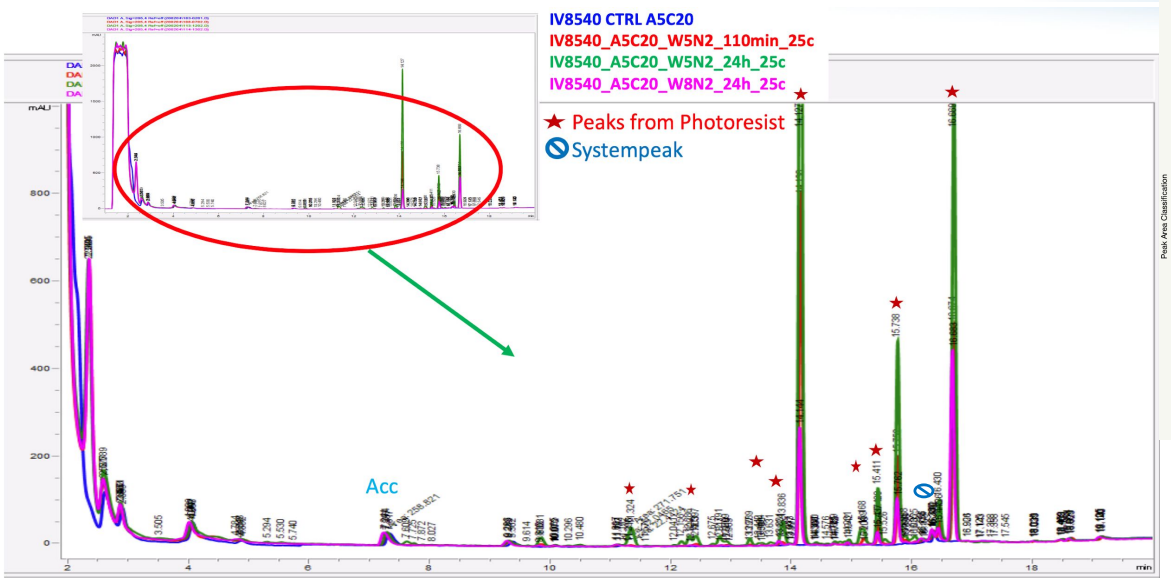
W1P1

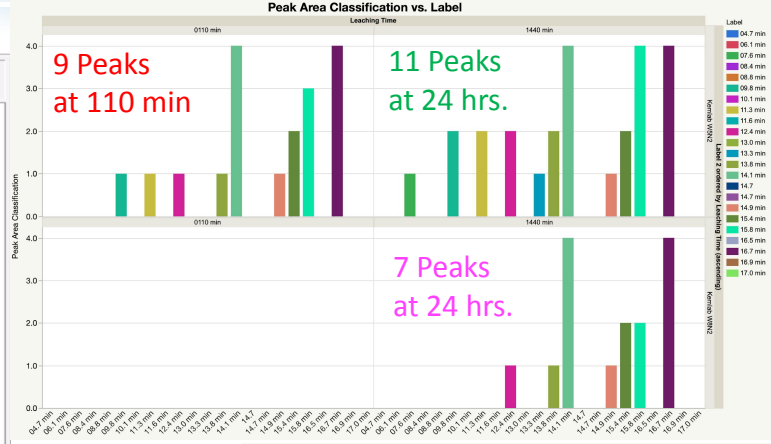


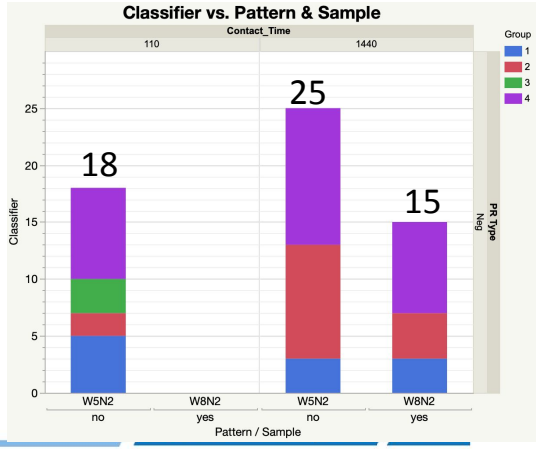
- With longer the contact time, both the number and intensities of PR-associated peaks are increasing.
- Leached amounts are clearly smaller than for the general purpose PR

Leaching Photoresist – Effect of exposure

W5N2 & W8N2

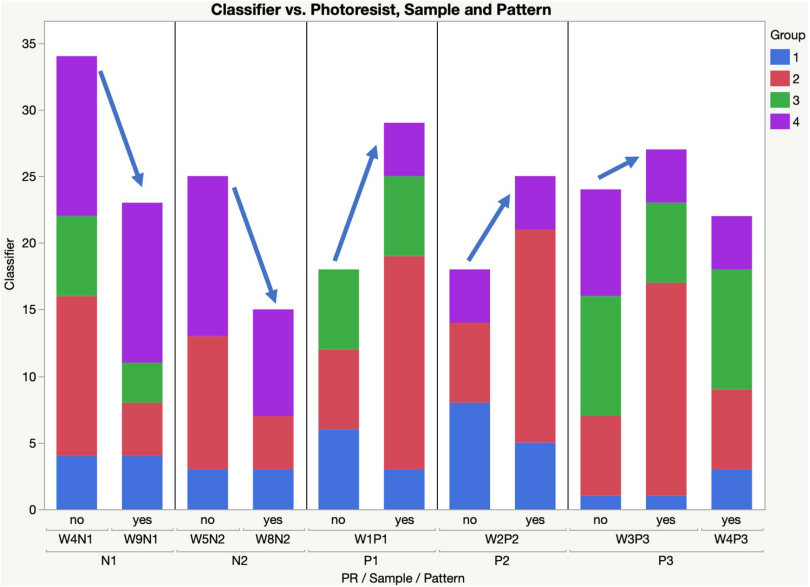






- PR-relevant peaks are scaling with the contact time.
- Similar peak distributions are seen for both cross-linked and as-coated materials.

Leaching Photoresist – General Trends



- KemLab materials compared favorably to the industry standard solutions with same/ lower amount of leaching
- Negative PRs show higher leached amounts (higher peak counts and intensities)
- Leached components are reduced for negatives PRs with exposure, and increase for positive PR
- Similar peak distributions are seen for both cross-linked and as-coated materials
- PEB experiment was inconclusive, and likely needs to be repeated

Summary and Outlook

- During packaging processing - access to both wafers and resist materials for method setup is both logistically and cost prohibitive
- We have developed a **proxy method** simplifying both material access and data processing using HPLC
- HPLC offers a powerful method of directly measuring the resist components leaching into the plating bath
- Methodology developed here may be used for detection of signs of PR in the plating bath
- The exact effect of these contaminants on the plating process can be understood deploying HPLC in conjunction with other techniques - like dynamic surface tension and electrochemical scans. More detailed investigation of electrochemical (EC) signals is our next topic