

# Understanding photoresist - electroplating bath interactions using HPLC methodology

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## Abstract

With the rapidly expanding range of design and integration flows required for advanced packaging, both foundries and OSATs alike are evaluating new types of materials for additive manufacturing - this is especially pertinent for both resist materials and galvanic plating baths. This problem is far from new (1), it is a part of the regularly required re-evaluation of process-material interactions (2) for the new packaging integration schemes, driven by changes in design, process flow, and technology requirements. With increasing demands for bath longevity and robustness of plating performance, material vendors are motivated to minimize interactions between the plating bath chemistries and photoresists, defining the plating pattern. In this study, we have evaluated the effect of several factors including - resist type (i.e. positive, negative, general-purpose vs "plating/package" type) and process parameters for both resist and bath material (by comparing several resist materials from different manufacturers with varying processing conditions on silicon wafers). We used reverse phase HPLC with UV-detection as a method of choice in this study to compare resist extractables into the galvanic baths. We utilized a copper plating packaging type galvanic bath as a representative bath material. We evaluated semi-quantitatively the extractable via their HPLC signature into the bath to compare resist properties and further attempt to extrapolate resist stability and breakdown magnitude with possible effects on bath life. The utility of the method developed here allows for comparing and quantifying (note - evaluation is semi-quantitative since no standard solutions of leached components exist) extractables via HPLC (high-performance liquid chromatography) allows for a better understanding of resist bath stability "factors", and can be further expanded into an online method for detecting early signs of bath contamination by a photoresist. It can also be used for aiding lithographers to better pre-assess photoresist capabilities and aid in the material selection for future plating applications.

## Keywords

galvanic plating bath, impurities, photoresist, electrodeposition, contamination control

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## I. Introduction

In recent years, with the advancement of new challenging semiconductor nodes and IC scaling with exponentially rising design and development costs, larger and larger emphasis is being placed on finding novel, creative and cost-effective packaging solutions [1]. At the same time, a range of applications and environments where

systems need to function is exploding, as IoT, self-driving vehicles, and AI become part of the mainstream users of high-speed, high-performance semiconductor devices. This adds additional new requirements to the properties and robustness of packaging materials and puts increased emphasis on advancing heterogeneous integration, previously referred to as advanced packaging. Right at the forefront of this advancement is the ability to reliably generate metallization stacks - be it copper pillars, bumps,

RDLs, or FanOut / FanIn structures, to which a galvanic electroplating process is one of the critical cornerstones. With recent advances in novel galvanic baths and new tooling platforms and form factors, the importance of plating process control is continually increasing and it becomes paramount for developing viable process flows and integration schemes [2]. This is especially true for high-performance and high-volume applications.

With the advancement of new packaging solutions, galvanic plating has been under continuous increased pressure to evolve and enable processes for both new structures (smaller pitch sizes, mixed pitches, and novel UBMs and stack materials), and new carrier form factors (as new size and standard panels are being introduced and adopted at HVM (high volume manufacturing)). All of that with improved throughput and without any performance degradation. Improving the plating process capability can not be done in isolation, and, as always, requires an integrated view of the overall process flow - with the plating hardware and materials interaction playing critical roles. Historically, the interaction between the photoresist material and plating bath chemistry has been an Achilles heel of the plating process - often suspected, but rarely confirmed. In the past, thick roll-on dry resist films have been utilized. They were fairly robust, and the main issue of the resist/plating process interaction was the resist film delamination, which can be initiated with chemical intrusion under the coated film, followed by its partial swelling. Current technology with reduced pitches and increased aspect ratios call for a novel, higher-resolution liquid resist materials. For those resists, polymer film interaction with the plating bath can lead to leaching components of the resist into the bath. Those interactions need to be taken into account as bump pitches decrease, leading to longer process times and reduced deposition rates [3]. To compensate and potentially increase deposition rates, elevated processing temperatures are often deployed. In combination, those two factors mean an increased impact on the resist materials and seed layers, and an increased risk of photoresist components leaching out and contaminating the bath. In this study, we explore the mechanisms of detecting leached photoresist components in the plating baths, by direct analytical measurement (HPLC).

Electroplating baths are complex aqueous systems with multiple components [4]) generally grouped into inorganic (metal, appropriate pH, and complexation agents) and organic additives (responsible for local control of the metal deposit morphology and geometry). Organic additives play a crucial role in bath performance and longevity during normal operation, as they are prone to partially decompose under the influence of electrolysis, or age naturally, contributing to breakdown products, degrading bath performance. Process conditions can also play a role, such as soft bake and exposure and of course resist type, along

with choice resin molecular weight and isomer content ratio (for the novolac based resins used in this study). Multiple components can leach out of the wafer due to bath and photoresist interaction. Resist interaction with aqueous systems has been studied extensively at the onset of the use of immersion lithography [6].

Here, we work on characterizing the mechanism and factors affecting resist leaching behavior, including: resist type, resist processing conditions as well as bath conditions and component concentrations. We seek to advance the knowledge and understanding of how the material properties can be characterized for both the formulator and the end-user in the plating bath. This study is the first one of several where we characterize factors influencing the intensity and negative side effects of such interactions utilizing an analytical HPLC technique.

The purpose of this initial work was to evaluate the feasibility of a photoresist stability/leaching study. As such, in this initial study, we did not apply voltage and/or plate-up metal on Copper wafers, but rather looked for comparative resist stability factors on coated silicon wafers exposed to varying conditions.

## II. Experimental

### A. Methodology

In this study, we have used the Agilent HPLC system in conjunction with Ancosys proprietary tooling for analyzing galvanic plating bath material before and after contact with the photoresist film. We took steps to optimize the wavelength used in the experiments to maximize the UV signal of the leached resist components, therefore increasing the sensitivity. Since access to the full stack patterned wafers at this stage of the semiconductor packaging process flow is cost-prohibitive, part of the methodology was dedicated to finding viable alternatives. Access to the resist film is also often complicated by multiple major OSATs and foundries utilizing material sets developed and manufactured exclusively for them. Thus, the “proxy” model system processes defined here, is meant to approximate the behavior of the processed resist film on the wafer while being a more easily attainable and understood set of materials.

*Plating bath.* A typical packaging process stack contains multiple metals plated in sequence. The exact sequence and amount of metal plated is, of course, specific to the final application, process flow, and material supplier. So are the galvanic plating bath materials, with specific inorganic components and proprietary organic additive concentrations. In this study, we deployed a commonly used in semiconductor packaging process flow Dow InterVia Cu 8540 copper galvanic plating bath. The harsh chemical

conditions of Copper Plating baths (i.e. low pH, high sulfuric acid content) provide a particularly challenging environment for photoresists. Thus - a typical packaging copper plating bath material, with and without organic additives was used.

*Photoresist.* Since the strength and impact of bath/photoresist interaction can be strongly influenced by the kind and specific properties of the photoresist - we have used several commercially available positive and negative photoresists. In this preliminary study, we looked at a variety of resists interacting with the copper plating bath chemistry to better understand the most critical factors and mechanisms. We have looked at both positive and negative from the different manufacturers, as well as exposed vs unexposed, low/ high soft bake) to find trends in resist leaching behavior.

*Positive photoresist.* For our positive working resist samples both a general-purpose and plating/package type resist were examined. One important consideration for a common novolac based resin resist is the Mw (molecular weight) and isomer ratio. Resist designers will generally evaluate a range of resins for both molecular weight and isomer ratio. One preferred embodiment for packaging resists can be a higher Molecular weight (Mw) i.e. of 20,000 g/mole plus with a high para content ratio. For stripping and/or removal often a lower molecular weight is desired, however for thicker films and the harsh chemical environment of a plating bath a higher molecular weight distribution is often preferred. Gel Permeation Chromatography (GPC) molecular weight comparisons can be an important design tool for the resist formulator when formulating packaging type plating resists. In this study, we also seek to correlate this molecular weight resin factor with potential leaching behavior in the plating bath.

*Negative photoresist.* The study also included several negative working photoresists. In this case, these resists were also based on novolac resins but feature a PAG (Photo Acid Generator) and a chemical cross-linker that, upon exposure and PEB (Post Exposure Bake), cross-links the coated resist film, greatly increasing its densification. In the negative working resist system, the exposed and cross-linked portion has upwards of a 10,000x lower dissolution rate than the unexposed, non-cross-linked portion. In addition to negative resist manufacturers, we also examined the effect of exposure on resist leaching behavior. To make the data sets as consistent as possible, we kept all the coated Film Thickness (FT) to approximately 10 microns. Factors, such as time in plating bath, were also looked at in this study.

*Processing conditions.* Processing factors like exposure and soft bake are included in the study with all resists coated on six-inch silicon wafers. Soft bake times

and temperatures can in particular be important factors for coated film densification. For example, a coated film that is too soft and less densified may be too permeable to the harsh plating bath solution. To help guard against this effect, often a post-processing “hard bake”, in addition to the post-exposure bake (PEB) is also done (i.e. at 110 Deg for 1 minute used here). It is being deployed to help further densify the feature prior to exposure in the plating bath. How densified the film or feature is, can also be a factor that contributes to an unwanted propensity for undercutting or undesirable feature lift-off, under these harsh bath conditions. The resist designer seeks to better understand these factors and minimize/eliminate this behavior in a packaging resist.

### B. Sample Preparation

All samples examined in this study were prepared (see procedure description) and then analyzed using the same HPLC reversed-phase method.

*Sample preparation procedure:* For the leaching experiments, a defined portion of copper electrolyte reference solution was poured onto the wafer and left on it for the selected contact time (110 min (short exposure) or 1 day (extended exposure)). Multiple electrolyte solutions were used - In order to be able to compare the different types of photoresist, a copper electrolyte reference solution was used, which contains both the typical inorganic components in common concentrations (VMS - virgin make-up solution) and the organic additives. All of the photoresists mentioned in this paper are listed below.

**Table 1:** Positive Photoresists

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

**Table 2:** Negative Photoresists

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

*C. Analyzing HPLC results: The Fingerprint Approach with Groups and Classifier*

Galvanic plating bath is a multi-component system with both organic and inorganic elements. Depending on the specifics of the bath formulation - some or all of the organic components, as well as their breakdown products in the bath can be UV active and therefore will be detectable in our HPLC analysis. In order to enable a comparative evaluation, and exclude the peaks associated with the bath itself, only the peaks that have arisen from contact with photoresists are considered in this analysis.

For a simplified comparative illustration of the measured photoresist related peak Groups and Classifiers were generated. This approach enables a fingerprint picture instead of total quantification of single peak areas. We outline and describe in detail the approach below.

**Table 3:** Definition of HPLC Peak Area Ranges

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

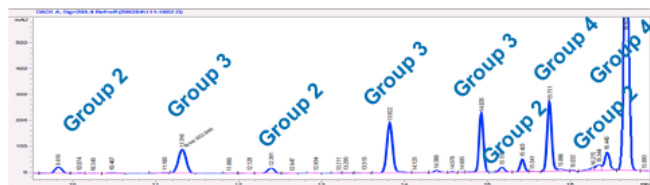
In this approach all the peaks detected (for example typical chromatogram is shown in Figure 1) were binned and summarised based on the peak areas. Table 3 summarises

the group assignments based on the peak areas measured. This type of summarization is necessary for the comparison of different solutions without an available standard of the extractable photoresist components and the possibility to absolutely quantify the amount of photoresist in the bath solution. Thus, the relative comparison is made for the purpose of the study.

In the process of chromatogram quantification - the peaks were first assigned to the group (based on peak areas) and then the whole chromatogram was characterized by calculating the correspondent classifier. The classifier is a calculated value, based on the number of the peaks of each group being detected.

- **Group** corresponds to Peak area classification at given retention time
- **Classifier** is calculated by summing up number of peaks counts multiplied by group identification factor (e.g.  $4 \times \text{Group 2} + 3 \times \text{Group 3} + 2 \times \text{Group 4} = 25$ )

Peaks present at the bath chromatogram prior to the introduction of resist material into it are omitted in this quantification. The calculated value of the classifier represents a measure of the total amount of extractable components for each photoresist.



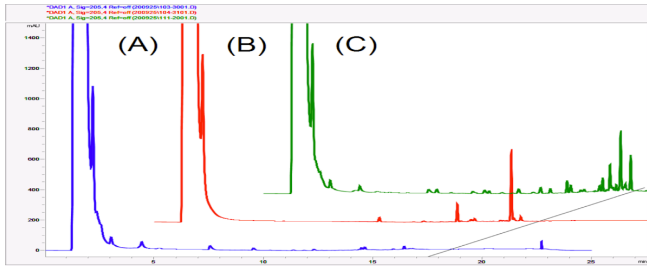
**Fig. 1.** Typical HPLC chromatogram of the bath solution with the photoresist contamination present and peak groups listed for all the peaks identified. Several small peaks (whose areas are smaller than 20 mAU) are not included in the summary and are ignored due to their low intensities.

**III. Observations**

*A. Positive Photoresists - effect of exposure*

After measuring the reference solution of a galvanic copper electrolyte without contact with a photoresist, we examined solutions that had been in contact with the photoresist at room temperature for 24 hours. Since we assumed that the inorganic constituents have a greater influence on the leaching behavior of the photoresists, we investigated this with VMS (virgin makeup solution, with fresh inorganic components only, with no organic additives). This testing was done with P1 - K-Pro15 resist material. The resulting chromatogram is shown by the red and green chromatograms in Fig. 2 for the resist-coated wafer in contact with VMS and full bath samples respectively. There are additional peaks in the rear part of the chromatogram with retention times greater than 13 min which can be assigned to the photoresists. The investigations with the full

bath solutions (green chromatogram, Fig. 2) show that the organic additives also interact with the photoresist and lead to numerous additional peaks.

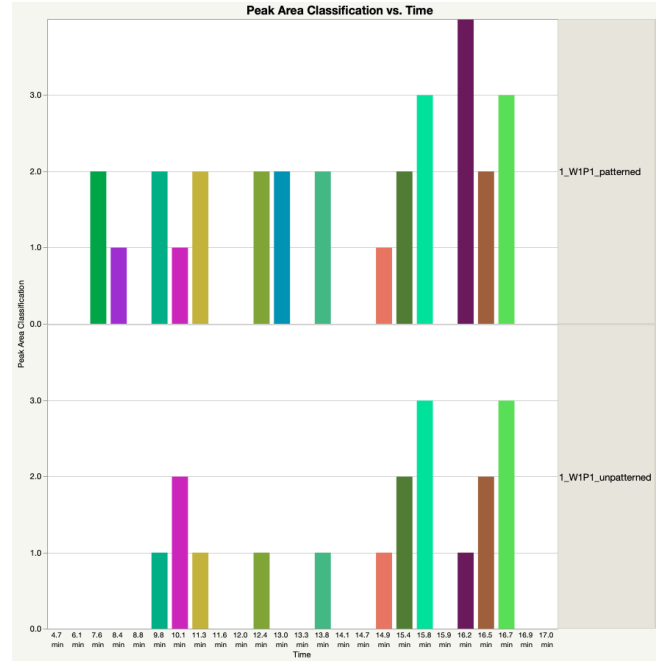


**Fig. 2 Chromatograms:** (A) Reference without contact to photoresist; (B) VMS on W1P1 (patterned) wafer for 1 day; (C) Full bath solution on W1P1 (patterned) wafer for 1 day

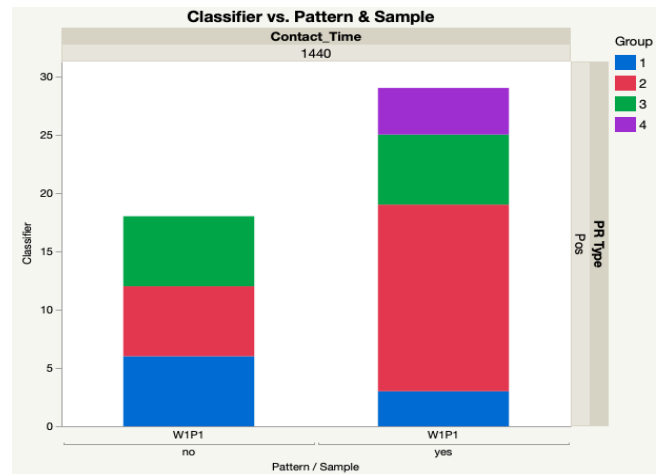
Studies with reference solutions show that more components leach out (higher peak area counts and more peaks) of the photoresist in the presence of organic additives and that some components have higher concentrations (larger peak areas). From leaching experiments with other additives, it can generally be established that peaks assigned to the additives can be increased or decreased after contact with the photoresist.

Positive-working photoresists become more soluble after exposure to UV radiation. These exposed areas are removed during the development process to form the final pattern on the wafer. We have compared the resist leaching as a function of resist film exposure (Figs. 3 (a and b)) and have observed higher proportions of the extractable photoresist components from patterned versus unpatterned wafers. Figure 3a shows a bar graph representation of the chromatogram, and 3b - summary of the peak area quantification (classifiers), comparing leaching out of the exposed vs unexposed wafer.

Clear differences between patterned and unpatterned wafers are highlighted in the classifier view in Figure 3b. A larger number of peaks of groups 1, 2, and 3, as well as an additional type of peak, not seen in the unpatterned wafer, are being observed. This observation is consistent with chemical reactions occurring in the patterned resist film during exposure and development - with the associated changes to the photo-active components in the film - generating fragments of smaller size / reduced molecular mass, more easily leachable into the bath solution. It is also consistent with the increased surface area of the patterned resist, compared to the as-coated film, that is immersed in the plating solution.



**Fig. 3(a) Classification of the peak area in groups:** Schematic representation of the chromatograms for W1P1 unpatterned wafer - below; W1P1 patterned above- above

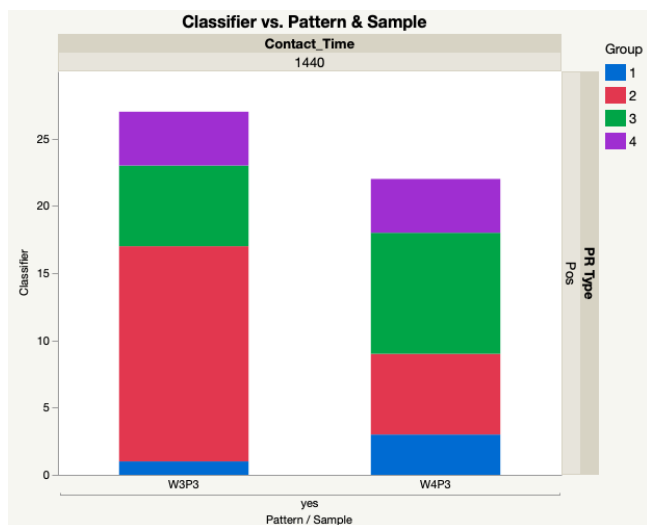


**Fig. 3(b) Classifier for comparison of different wafers:** W1P1 unpatterned - left bar; W1P1 patterned - right bar

*B. Positive photoresists - Effect of the soft bake*

Optimal process control in the lithographic process is important for the durability of the photoresist layer. Deviations from normal processing related to the lithographic track excursions - like bake temperature fluctuations, develop time and duration variability can drastically affect pattern definition and have a profound effect on downstream processing. Here we looked at the effect of the resist bake temperature deviation from the

standard and the effect of bath contact duration. A wafer W3 with photoresist P3 (KL6008 material) was soft baked (also known as post apply bake or PAB, labeled here as SB) at 115 °C for 3.5 min and another wafer W4 with the same photoresist was treated at 105 °C for 2.5 min. We were able to show that only these small changes in the soft bake process in terms of temperature and duration lead to small but measurable differences in leaching product distributions.



**Fig. 4 Classifier for comparison different wafer:**  
W3P3 patterned (SB115°, 3.5') - left bar;  
W4P3 patterned (SB105°, 2.5') - right bar

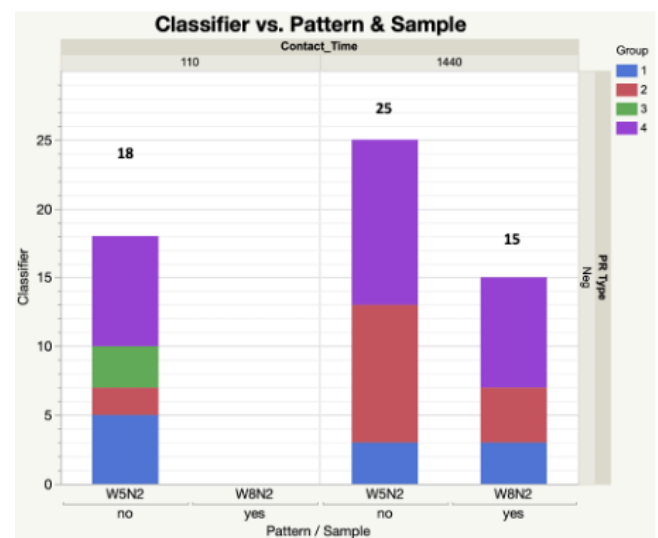
Figure 4 shows the results of this experiment. Based on the general knowledge of polymer science, higher bake temperature and longer bake time should lead to better resist densification and possibly more outgassing of the volatile components. This, in turn, should lead to less leaching out of the resist film. However, in this single wafer experiment, the observations are the opposite of the expectations of hotter baked/outgassed film leaching less. To get a definitive understanding and confirmation of this observation, it should perhaps be repeated in a more statistically meaningful way, with larger sampling. This observation, however, can not be generalized for all positive resists, as the specific bake temperatures and rest of processing conditions are always closely tied to the resist composition (solids loading, solvent type), as well as desired resist profile on the wafer (often a PAB / PEB regime and develop process steps are co-optimized for the desired performance for a specific application and on-wafer stack).

### C. Negative Photoresists

In this study, we always observed relatively larger amounts of leached photoresist components for negative compared to positive photoresists. The longer the contact

time (wafer contact with the bath electrolyte), the more signals regarding contamination are visible. On exposed patterned cross-linked wafers the photoresist layer is more stable and shows less effect of wafer/bath contact time. In the case of non-exposed/non-cross-linked negative resist - a somewhat expected result, based on the general understanding that negative photoresists are bulk-cross-linked and in this way partially passivated and protected from the electrolyte attack during contact time.

The investigations regarding the contact time of the unpatterned wafer with the copper electrolyte clearly show that the concentrations and number of peaks increase with increasing contact time. The following statement emerges from the right-side of Fig. 5. The peaks to be found in the chromatogram of the patterned wafer sample are also visible in the chromatogram of the unpatterned wafer sample with the same retention times. However, the chromatogram of the unpatterned wafer sample has additional peaks. This is consistent with residuals of the casting solvent still and other components, still being present in the film before patterning, and being removed during the PAB/PEB / pattern and development stages.



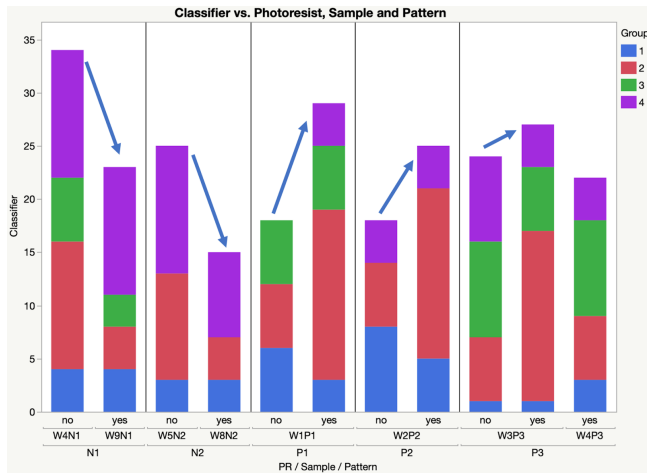
**Fig. 5 Classifier for comparison different wafer:**  
W5N2 unpatterned for 110 min - left bar;  
W5N2 unpatterned for 1 day - middle bar;  
W8N2 patterned for 1 day - right bar  
Note\* : No data is available for W8N2 110 min

Fig. 5 clearly shows that the unpatterned negative photoresists are more unstable the longer they are in contact with the copper electrolyte. However, the patterned wafer is still significantly more stable after one day of contact compared to the unpatterned wafer after only 110 min of contact.

#### D. Comparison of different Photoresist Types

Photoresists (both positive and negative) from several resist manufacturers have been compared in this study. The leaching behavior of the KemLab materials was compared to the industry standards and was used as the basis for this comparison. General trends and a summary of the observed behavior are shown in Figure 6. Of note is the fact that the negative photoresist APOL-LO 3207 from KemLab (N2) shows improved leaching behavior, compared to the industry-standard competitor.

Negative photoresist types (non-exposed) show higher peak intensities in the leaching experiments than positive photoresist types. This is consistent with the negative photoresist types having lower leaching behavior after UV exposure, and positive photoresist types having a slightly higher leaching behavior after UV exposure.



**Fig. 6 Classifier Variability Chart of all wafers investigated in this study grouped by**

- photoresist type (N1, N2, P1, P2, P3)
- sample (W4N1, W9N1, W5N2, W8N2, W1P1, W2P2, W3P3, W4P3)
- pattern (yes, no)

From the point of view of resist design, the following general trends are known and can be confirmed based on the findings in this study:

- Patterned cross-linked negative photoresists mostly show less leaching behavior than positive photoresists.
- Exposed and patterned negative photoresist (W9N1, W8N2) show less leaching than non-exposed negative resists (W4N1, W5N2).
- Positive resists should not show a significant leaching difference with exposure, because this part would be washed out before plating use. Nevertheless, there is less leaching with non-exposed wafers.
- Effect of soft bake on leaching behavior on positive resists indicates a slight difference in signature peaks as

a function of soft bake (W3P3 vs W4P3).

- Comparison of general-purpose positive resist (P3) vs positive packaging type resist (P1) shows less leaching with packaging type resist.
- When comparing KL resists with other manufacturers, the negative KL resists APOL-LO 3207 (N2) has a better performance/stability in leaching behavior. The positive packaging type resists K-Pro15 (P1) shows comparable performance/stability in leaching behavior compared to other manufacturers P2.

### III. Conclusions

HPLC measurements of galvanic baths provide an insight into the leaching behavior of photoresists. A comparison of negative and positive working photoresists showed that the HPLC signature differs, i.e. there are components that only occur in negative photoresists and vice versa. Additionally, differences due to conditions (e.g. leaching time, soft bake) can be confirmed. Our work aims to make the described novel analysis approach of monitoring galvanic baths a useful tool, both for the development of new materials (i.e. galvanic baths, photoresists) as well as stack optimization, to help reduce photoresist leaching, and potentially improving plating bath life in volume production. We further surmise that the characterization is in line with the expected results. The measured values and their trends give encouragement and validity to the stated goals of monitoring photoresist stability and reducing the extent of its impact on plating bath, with the ultimate goal of improving plating bath lifetime and reducing on-wafer defectivity.

Mechanisms and effects of resist leaching and their effect on the plating bath performance are additional critical questions to be answered and understood. To help further this understanding we are planning to answer the following questions in our next studies [5]:

- How is the behavior of the additives used in the electroplating bath influenced by photoresist contamination?
- What influence do the photoresist impurities have on the properties of the electrochemical deposits?
- Can a practical correlation between photoresist contamination/degradation and defects on product wafers be derived?
- What influence do production conditions such as throughput and variety of wafer types (different open areas, wafer count, contact times) play?
- Can electrochemical or other forms of detection be used and correlated to leaching results as well.
- Can this approach be used for other types of galvanic baths?

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