### **Embracing Evolution: Photoresist Stripping 2.0**

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### **ABSTRACT**

Photoresist stripping is an integral part of the wafer-level manufacturing process. This is the step in which the photoresist, which is used as a template for the Cu post electroplating process, is removed using a solvent. Failure to properly strip the wafer can result in critical defects such as residual resist, discoloration and contamination leading to low yield and can compromise package integrity through electrical defects such as shorts. With rising raw material prices and the introduction of more complex technologies/patterns, one of the biggest challenges in the semiconductor industry is how to balance cost and quality while maintaining operational excellence.

In this paper, the team has discussed how all of these metrics were positively impacted through breakthrough solutions for the Photoresist Stripping Process, highlighted throughout this strategic methodology: exploring all options, stripping the process down to its basic principles, removing non-valueadded steps, and embracing process flexibility by challenging current specifications. Together, these initiatives helped to deliver chemical cost savings of up to 10% per annum, with the opportunity for a further 10% per annum through fan-out projects, an additional 25% increase in tool throughput and supplier coverage alongside three fundamental baseline studies that could provide the future for further improvements.

#### **1.0 INTRODUCTION**

The photoresist in wafer level manufacturing is a uniformlycoated material on the surface of a substrate that is exposed and developed to create a pattern based on required circuit design.

After the Cu is electroplated onto this pattern, photoresist is no longer needed and is thus removed through the photoresist stripping process – a spray solvent process that dissolves the photoresist until completely removed from the wafer. This process is simplified in Figure 2. After this, the substrate is sprayed with isopropyl alcohol and water to completely remove chemical residues. It is critical that each process step is reviewed as failure to do so could affect the efficiency of Photoresist Stripping. One such instance is a non-conformance instance reported last December 2020, which when the team assessed, is due to a tiny metal causing EOS damage. Upon investigation and reviewing lot history, this tiny metal residue was caused by an organic material – photoresist residue - that hindered the etching out of excess intermediate thin metal. This has pushed the team to develop the Swell Test and optimize the process through wafer spin speed augmentation which lead to an improved photoresist stripping efficiency and an overall stable process<sup>1</sup>.



Figure 1. Top view of unit from customer complaint



Figure 2. Diagram showing the substrate before and after Photoresist Stripping where PR is short for "Photoresist".

However, there are also external critical factors outside of the process steps affecting process stability – especially when constrained in terms of supply delivery, chemical availability, and keeping up with increasing demand. The photoresist stripping process was affected – with multiple line down occurrences. As more complex devices appear – this brings forth a pressing need to update the process steps to support line and continue production. This is on top of the challenge to lower operational cost and achieve higher productivity metric.

In this paper, the team has highlighted the strategic methodology, and the breakthrough solutions in effect to

following this flow, that has significantly helped prepare the Photoresist Stripping process for future development.

### 2.0 REVIEW OF RELATED WORK

Coming to an era where the competition for new technology especially for the chip industry is becoming more aggressive<sup>2</sup>, in parallel to the need to improve product design is the need to elevate innovation inside the chip manufacturing plants - Wafer-level manufacturing plants, to be particular. By detailing findings specific to the spray solvent procedure for photoresist removal that have not yet been covered in other academic works, this research helps fill in this gap. One study that has been detrimental in supporting the viability of this paper is the article on the effect of wafer rotation of Photoresist using supercritical carbon dioxide<sup>3</sup>. It was claimed here that increasing the RPM increases photoresist removal efficiency due to improvement in velocity profile, correlating with the researchers' previous study on effect of RPM to the spray solvent process<sup>1</sup>. Another is the evaluation on the bath life effects of photoresist removal that has stressed the dependence of the dissolution process to the reactivity of the quaternary ammonium hydroxide<sup>4</sup> - which is directly related to the chemical pH. This claim helps back up the team's findings that, provided certain variables are under control, bath life and other parameters can be further optimized. These are some of the fundamental studies the researchers have reviewed among all other studies about the dynamics of the photoresist removal process that have significantly influenced the new findings discussed in this paper.

### **3.0 METHODOLOGY**

As the Photoresist Stripping Process has been optimized multiple times, the researchers' challenge is to develop a plan to further enhance; as a result, these strategic methodologies were developed.

### 2.1 Materials

These are the resources the researchers used to support the experiment designs:

- Strip Single Wafer Processing Tool
- Validation Wafers
- Plating Lab Peripherals
- Optical Inspection Tools: Microscope and AOI

#### 2.2 Exploration of All Options

Everything starts with Phase 0 – which is a step outside of the process. For this circumstance, the researchers reviewed all options for alternative suppliers. After assessment, it was decided to concentrate on Isopropyl alcohol supply due to the following reasons: (1) leadtime constraints due to international logistics, (2) one of the top cost contributors, (3) seeing a gap on academic research on significance of specific

IPA parameters. Table 1 lays out all the parameters the researchers have monitored to evaluate new IPA supply. In addition to these variables, product performance throughout production has also been evaluated and contrasted with control lots.

Physical Properties	<b>Chemical Properties</b>	Allowable Ion Content	Other Impurities
Density	Acidity	Chloride (Cl)	Boron
Assay (CH3CHOHCH3)	Alkalinity	Phosphate (PO4)	Lead
Color	Water	Nitrate (NO3)	Other metals
	Residue after Vaporzation	Sulfate (SO4)	

## Table 1. IPA Chemical Properties that Could Potentially Affect Post-stripping Cleaning Efficiency

### 2.3 Stripping the Process to its First Principles

The next stage after taking in the wide picture is to zoom in on the specifics of the process and break it down into elements, or first principles, that have an impact on the desired metrics, which in this case is cost. By definition, First Principle is a term used to describe an element that cannot be broken down to smaller constituents. Figure 3 lists all the first principles that have an immediate impact on the metrics of the Photoresist Stripping Process. The boxes in green are the topics discussed in this paper.



Figure 3. FTA (Fault Tree Analysis) of the Photoresist Stripping Process and the Factors that Directly Affect Cost and Productivity

#### 2.4 Removing Non-value-added Steps

The next step in the evaluation process, after identifying the relevant factors and optimizing, is to see if there are any elements that, if eliminated, would still provide the same outcomes. Here are some of the things the researchers determined to be "non-value added," supported by study and feasibility data: (1) IPA cleaning Step post-NMP for non-multimetal stack devices (2) High pressure pumps (3) side rinses. The physical characterization table for assessing feasibility outcomes is shown in Table 2.

The viability of a process modification is determined by these crucial criteria: (1) good visual inspection and SEM surface elemental analysis results after stripping and etching, (2) good AOI yield (3) low underetch DPPM indicating low photoresist residue. Underetch is a defect similar to the issue on Figure 1. Results were then compared to a baseline/control lot to see if they are comparable to the standard approach, guaranteeing that the quality is the same.

Table 2. Physical Characterization Table Used to Assess Results of Process Change

				2		
Evaluation	Post-Strip Visual Inspection	Post-Strip SEM	Post-Etch Visual Inspection	Post-Etch SEM	AOI Yield	Underetch DPPM
Baseline Lot - w/ complete IPA Rinse						
Leadlot - IPA Rinse Removed						
Baseline Lot - w/ IPA Side Rinse process						
Leadlot - IPA Side Rinse Removed						
Baseline Lot - utilizing high pressure pump						
Leadlot - High Pressure Pump Removed						

### 2.5 Process Flexibility: Challenging the Norm

Once all the factors have been optimized and all non-valueadded products have been removed according to allowed standards/specifications, the last step is to seek if these standards can be further stretched. As the sector transitions to increasingly complicated technologies, the researchers believe that there is an increasing need to question conventional wisdom. The following projects have been prompted by this initiative: (1) Assessing a different grade of IPA, (2) Studying Photoresist compatibility in a mixed bath and factors that affect bath life. These projects seek to push the limits of the process.

### 2.5.1 Assessment of a Different-Grade IPA Chemical

The first project was evaluated using the criteria from Table 1, which contrasted the new, different-grade supply with the existing supply. To enable the switch, the discrepancies were documented, and some more controls were introduced on the supplier's end.

# 2.5.2 Baseline Study on Photoresist Compatibility and Factors that Affect Bath Life

After examining the crucial elements that determine bath life, the second study seeks to comprehend the Photoresist Stripping Process. It has two functions: first, it studies various correlations and important factors to potentially increase bath life; second, it satisfies the need for a better understanding of process capability to serve as a foundation for incoming complex technologies, which may require a different kind of resist to be qualified. Table 3 displays the experimental design followed to assess mixing of Resists A, B, C and D. The researchers chose to concentrate on pH and density for this design as these appear to have the most impact based on research<sup>4</sup>. Table 4 shows the difference of the Resists in terms of active components.

### Table 3. Experimental Design to Study Photoresist Compatability and effect of pH and density across Bath Life

Cullt	Amount of re	sist based o	pH	data	Donsity		
Spiit	Resist A	Resist B	Resist C	Resist D	pH	Temp	Density
1	0	0	0	0			
2	100%	0	0	0			
3	0	100%	0	0			
4	0	0	100%	0			
5	0	0	0	100%			
6	40%	20%	20%	0			
7	40%	20%	20%	20%			
8	40%	20%	0	20%			
9	0	0	50%	50%			
10	25%	25%	25%	25%			
11	60%	0	20%	0			
12	60%	0	0	20%			
13	60%	0	20%	20%			

# Table 4. Difference of Resists A, B, C and D in terms of active component.

Photoresist	Photoactive compound	Resin	Solvent	
Resist A	DNQ	Novolak	PGMEA	
Desist P	DNQ	Novolak	DCMEA	
Kesist B	Photoacid generator	other resins	FOMEA	
	DNQ	Novolak	PGMEA	
Resist C	Photoscid generator	Acrulic type	3-Methoxy butyl	
Resist C	i notoaciu generator	Activite type	acetate	
		Polyhydrostyrene		
Pagist D	DNQ	Novolak		
Photoacid generator other resins		FUMEA		

### 4.0 RESULTS AND DISCUSSION

### 4.1 Assessment of Alternative IPA Suppliers

The main purpose of the IPA cleaning process is first, to act as an intermediate cleaning step between stripping chemical and DI Water, and second, to clean off any remaining chemical residue on the delicate patterns. Therefore, the main concerns are its efficiency in cleaning and its purity to ensure that delicate circuitry is not damaged. The researchers have qualified a new IPA supplier costing ~8% less than the current supply. Table 5 shows the difference in parameters of the new supply evaluated compared to the current supply.

# Table 5. Comparison of New Supplier IPA Properties inreference to Current Supply

Physical Properties	New Supplier	Allowable Ion Content	New Supplier
Density	0.5% lower	Chloride (Cl)	same
Assay (CH3CH0HCH3)	0.15% higher	Phosphate (PO4)	same
Color	same	Nitrate (NO3)	same
Chemical Properties	New Supplier	Sulfate (SO4)	same
Chemical Properties Acidity	New Supplier same	Sulfate (SO4) Other Impurities	same New Supplier
Chemical Properties Acidity Alkalinity	New Supplier same same	Sulfate (SO4) Other Impurities Boron	same New Supplier same
Chemical Properties Acidity Alkalinity Water	New Supplier same same same	Sulfate (SO4) Other Impurities Boron Lead	same New Supplier same higher by 50%

### Table 6. Production Monitoring Results of Evaluation Lots at Different IPA Mixtures of Old and New Supply

	Data Gathering						
IPA Composition	Visual Inspection	Shear	AOI Yield	Probe			
20% old - 50% new	no abnormalities	good	comparable to baseline	good			
60% old - 80% new	no abnormalities	good	comparable to baseline	good			
100% new	no abnormalities	good	comparable to baseline	good			
20% new - 50% old	no abnormalities	good	comparable to baseline	good			
60% new - 80% old	no abnormalities	good	comparable to baseline	good			
100% old	no abnormalities	good	comparable to baseline	good			

Table 6, on the other hand, shows the performance of the evaluation lots across production at different mixtures of old and new supply. From above data, these can be concluded: (1) quality is the same at ~1% difference in terms of assay and density, and 50% higher metal impurity in terms of ppb, (2) it is feasible to mix old and new supply – at any mixture, outcomes is the same. This is possibly because though the new supply has higher impurity, it is not enough to damage the delicate circuitry. Thus, as there is not much academic research on the flexibility of using IPA as a cleaning agent in the semiconductor industry, these findings could be a precursor to explore lower assays to optimize post-strip cleaning process. This was also the motivation for the team to look for a lower-cost, different grade IPA which will be discussed later in this paper.

### 4.2 Process Optimization

As seen on Figure 3, one significant factor that affects cost is the wafer spin speed / RPM during the dissolution step. Wafer rotation affects the photoresist stripping efficiency by improving the velocity profile of wafer spin. When rotation is increased, bulk photoresist is easier to spin-off. This has been extensively discussed on the researchers' previous study on Swell Test<sup>1</sup>. This time, the process change was fanned out to a different chemical supplier but still NMP-based, further proving the theory of wafer rotation on same NMP-based stripping chemicals. By finding the best RPM, engineers were able to reduce the drain time by 20%, thus reducing chemical cost as well. This is seen on Table 7 where at high RPM and lower time (mid+RPM, mid+time) the % resist removal is comparable if not better to baseline (low RPM, high time).

## Table 7. Percent Removal of Bulk Photoresist at Increasing Time and Increasing RPM

		Time				
		high	mid+	mid	low+	low
	low	50%		5%		
	low+	70%		5%		
KPIVI	mid	95%	10%	5%	1%	<1%
	mid+	99%	60%	10%	1%	<1%
	high	97%		10%		

### 4.3 Removal of Non-Value Added Steps

The findings on impact of wafer rotation has enabled as well the removal of non-value added operations, as seen on Table 2. By increasing the RPM, it is no longer necessary to use a side rinse<sup>1</sup> given good production results (see Table 8). Optimizing the RPM, on top of some changes on the process steps, removed as well the requirement for a high pressure pump that utilizes 16 times the pressure of regular pumps.

Table 8. Production Monitoring Results on Projects Involving Removal of Non-Value Added Steps

Evaluation	Post-Strip Visual Inspection	Post-Strip SEM	Post-Etch Visual Inspection	Post-Etch SEM	AOI Yield	Underetch DPPM
Baseline Lot - w/ complete IPA Rinse	no residual resist	No traces of organic matter	no underetch	No traces of organic matter	good	good
Leadlot - IPA Rinse Removed	no residual resist	No traces of organic matter	no underetch	No traces of organic matter	comparable to baseline	comparable to baseline
Baseline Lot - w/ IPA Side Rinse process	no residual resist	No traces of organic matter	no underetch	No traces of organic matter	good	good
Leadlot - IPA Side Rinse Removed	no residual resist	No traces of organic matter	no underetch	No traces of organic matter	comparable to baseline	comparable to baseline
Baseline Lot - utilizing high pressure pump	no residual resist	No traces of organic matter	no underetch	No traces of organic matter	good	good
Leadlot - High Pressure Pump Removed	no residual resist	No traces of organic matter	no underetch	No traces of organic matter	comparable to baseline	comparable to baseline

Another non-value step identified was the Post-stripping cleaning using IPA. Following stripping with NMP chemical, IPA is mostly used to get rid of any remaining stripping chemical residue before the wafer is rinsed with DI water. For multimetal stack devices, IPA is a crucial intermediary step to prevent galvanic corrosion<sup>5</sup>. IPA stops NMP and DI water from coming into direct touch, eliminating the possibility of a galvanic cell arrangement. TI has a range of devices - some with multimetal stack posts and some with only one type of metal post. Galvanic corrosion is not a problem for the latter, thus it is possible to entirely do away with IPA post-stripping rinsing and replace it with DIW. These non-multimetal stack devices account for more than 60% of the production pipeline and removal of IPA will greatly contribute to reducing chemical usage and in effect, enable chemical cost reduction. Table 9 shows the evaluation results of removing IPA in terms of Visual Inspection, Undercut, FTIR, SEM Elemental Analysis. This evaluation was also done across stripping tank bath life and no negative progression on any parameter was seen. A saturated IPA tank is the worst case scenario but still yielded good results based on Table 9. Results show that even if IPA rinse is removed, outcome is still the same - no corrosion is seen and SEM analysis also show no presence of organic contamination or oxidation. This study also demonstrates that DI water is sufficient to remove NMP residue because both have the same composition and polarity, making them both suitable solvents for NMP.

### Table 9. Production Monitoring Results on Removing IPA Rinse after Stripping w/ NMP-based chemical (Nonmultimetal stacks)

	Visual Inspection	Undercut	FTIR	SEM EDX	Composition
Baseline - w/ IPA rinsing		<5% difference	no presence of organic contamination	$\bigcirc$	100% Cu
Leadlot - IPA Rinse Removed		<5% difference	no presence of organic contamination	$\bigcirc$	100% Cu

### 4.3 Assessment of A Different Grade IPA Chemical

Having assessed a new IPA supplier with higher impurity but still producing good production outcomes, this gave the team the notion to evaluate the possibility of a different grade, lowcost IPA mainly to help resolve the problem on leadtime constraints with cost as secondary consideration. One of these is a supplier discovered to have laxer IPA production regulations. Table 10 shows the difference of the "new supplier" discussed previously in this paper versus the "different grade" supply in terms of properties. Most prominent in this table is the significant difference in terms of color, residue after vaporization, chloride, phosphate and Lead content. Despite higher impurities, the chemical has been qualified and no issues has been seen on production to date after almost one year of running - design and results are similar to Table 6. Not studied in this paper, as testing per parameter is quite costly, is an experimental design to thoroughly examine each property by increasing/decreasing the value in order to get the minimum and maximum parameter value allowable. It is also worth to note that the team has added an additional control of COA (Certificate of Analysis) Review every batch sent to the plant for sanity check.

### Table 10. Chemical Properties of "New Supplier" IPA and "Different Grade" IPA in comparison with Current Qualified Supply

PARAMETERS	New Supplier	Different Grade
Physical Properties		
Density	0.5% lower	not stated
Assay (CH3CHOHCH3)	0.15% higher	0.3% lower
Color	same	60% higher (APHA
Chemical Properties		
Acidity	same	same
Alkalinity	same	same
Water	same	same
Residue after Vaporzation	same	33.3% higher (ppb)
Allowable Ion Content		
Chloride (Cl)	same	60% higher (ppb)
Phosphate (PO4)	same	300% higher
Nitrate (NO3)	same	not stated
Sulfate (SO4)	same	not stated
Other Impurities		
Boron	same	
Lead	higher by 50%	higher by 400% (ppb)
Other metals	same	

# 4.4 Baseline Study on Photoresist Compatability and Factors that Affect Bath Life

The stripping chemical is recycled during photoresist stripping up to a specific bath life. Depending on the needs of the device, various photoresist types are blended during this cycle. As a result, there is a growing need to investigate the impact of mixing these resist types and to learn how to effectively manage the procedure by identifying the critical variables that influence stripping efficiency. Since studies have shown that the reactivity of the bath is directly correlated with the concentration of ammonium hydroxide<sup>4</sup>, which can be detected by pH, researchers have chosen to concentrate on this issue. The more alkaline or the higher the pH, the more photoresist can be dissolved by the bath.

Figure 4 displays how pH affects the ratio of different resists A, B, C, and D – in reference to splits from Table 3. Each split has three bar graphs, corresponding to measurements taken at 0, 30, and 60 minutes after mixing. Here it is seen how different resist types affect the pH of bath, specifically split 4 – containing 100% Resist C – which from Table 4 has a unique composition compared to other resist types which could possibly contribute to larger bath degradation by making the bath more acidic. Aside from these variables. sludge formation was also monitored at time 0 to 5 days and no sludge/by-product formation was observed - which is expected because all the chemicals from Table 4 are similar in polarity. DNQ stands for diazonaphtoquinone while PGMEA stands for propylene glycol methyl ether acetate. All of the known components of the photoresists contain polar groups, and NMP, contains a polar methyl-substituted amide group which also makes it polar. Therefore, dissolution of resist components in NMP is favored by the similarity in polarity.

Oversaturating the bath was also assessed as seen on Figure 5 and interestingly, bath alkalinity has increased in general compared to Figure 4, but still more acidic than baseline. These findings show that there is a strong correlation of pH and amount of resist in bath – which if further studied could help the researchers establish a proper model to evaluate at what pH the bath is still useable. Because of these findings, researchers can also conclude that there should be no problems mixing the current resist types in a bath – helping significantly with lot cycle time reduction. For density, the results are inconclusive which is why it is not focused on – based on initial data, density is not affected or probably negligible across all splits.



Figure 4. Results of Experimental Design on the Effect of pH and Density at Different Bath Ratios of Photoresist Types



Figure 5. Results of Experimental Design on the Effect of pH and Density at Different Ratios of Photoresist Types – simulation of saturating the bath 3x larger than normal.

### **5.0 CONCLUSION**

As the business grows more aggressive in terms of innovation, manufacturing facilities must evolve in a similar manner. Targeting cost and productivity metrics, and understanding the process are the key to ensure that we have enough room to cater for the emergence of newer and more complicated packages. For this, the researchers have demonstrated their strategic approach: Exploring all options, Stripping the process down to its basic principles, Removing non-value-added steps, and embracing process flexibility by specifications. challenging current Through this methodology, the following breakthrough solutions were achieved: Wafer spin speed optimization, Removal of nonvalue added steps like side-rinsing and high pressure pump, Removal of Post-strip IPA Rinsing, Qualification of two new IPA suppliers – one low-cost alternative, one different grade, and lastly, a Baseline study on photoresist compatibility and effect of pH on bath life.

These are the main lessons learned from these initiatives: The impurities and chemical assay are the most crucial factors to evaluate while vetting alternative sources for cleaning solvents like IPA for the semiconductor industry. In order to find an even more affordable option, it is possible to investigate a lower assay and investigate looser restrictions for metal impurity. Prior to optimizing a process, it is crucial to identify the variables that influence the desired metrics. In this instance, a reduction in chemical costs is directly attributed to wafer spin speed. The bulk of the photoresist is easier to spin off as the wafer spin speed rises, which reduces drain time and thus, chemical usage. Through optimizing the RPM, these non-value added steps were also removed: IPA side-rinsing and usage of a high pressure pump. The total removal of IPA rinsing post-stripping for non-multimetal stacks was another non-value added process evaluated. According to research and positive evaluation results, it is possible to eliminate IPA for these devices. Without generating corrosion or leaving behind organic contaminant residue, DI water is sufficient to eliminate NMP residue. In a lab-scale setting, the impact of pH and density on bath life was also investigated. This led to the discovery of a significant correlation between pH and the addition of photoresist, which might serve as the foundation for a model to predict bath life based on pH and perhaps other significant parameters not covered in this study. Through this finding it was also confirmed that it is feasible to mix the current resist types without negative reactions. Together, all these initiatives had the following effects on metrics: up to 10% annual chemical cost savings, with the potential for an additional 10% per year through fan-out projects; an additional 25% increase in tool throughput; 2 new IPA suppliers; and three fundamental baseline studies that could pave the way for future advancements.

### **6.0 RECOMMENDATIONS**

The researchers provide some recommendations after having the chance to evaluate the Photoresist Stripping procedure from Phase 0 to completion. These recommendations have not been explored because of limitations and priorities. First, it is advised to develop an experimental design for each parameter to simulate failure when evaluating a new IPA cleaning solvent, specifically to establish the range of permissible assay and allowable impurity values. Another future plan is to use statistical tools to build a model for photoresist compatibility. In order to fully comprehend bath life, it is also advised to further investigate other factors outside pH, such as conductivity for organic material concentration, color, and density.

### 7.0 ACKNOWLEDGMENT

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