Aqueous-based thick photoresist removal for bumping applications

John C. Moore*, Alex J. Brewer, Alman Law, and Jared M. Pettit
Daetec, LLC, 1227 Flynn Rd., Unit 310, Camarillo, CA 93012

ABSTRACT

Cleaning processes account for over 25% of processing in microelectronic manufacturing [1], suggesting electronics to be one of the most chemical intensive markets in commerce. Industry roadmaps exist to reduce chemical exposure, usage, and waste [2]. Companies are encouraged to create a safer working environment, or green factory, and ultimately become certified similar to *LEED* in the building industry [3]. A significant step in this direction is the integration of aqueous-based photoresist (PR) strippers which eliminate regulatory risks and cut costs by over 50%. One of the largest organic solvent usages is based upon thick PR removal during bumping processes [4-6]. Using market projections and the benefits of recycling, it is estimated that over 1,000 metric tons (mt) of residuals originating from bumping processes are incinerated or sent to a landfill. Aqueous-based stripping would eliminate this disposal while also reducing the daily risks to workers and added permitting costs. Positive-tone PR dissolves in aqueous strippers while negative-tone systems are lifted-off from the substrate, bumps, pillars, and redistribution layers (RDL). While the wafers are further processed and rinsed, the lifted-off PR is pumped from the tank, collected onto a filter, and periodically back-flushed to the trash. The PR solids become a non-hazardous plastic waste while the liquids are mixed with the developer stream, neutralized, filtered, and in most cases, disposed to the sewer. Regardless of PR thickness, removal processes may be tuned to perform in <15min, performing at rates nearly 10X faster than solvents with higher bath lives. A balanced formula is safe for metals, dielectrics, and may be customized to any fab.

Keywords: thick photoresist, aqueous, bumping, lift-off,

1. INTRODUCTION

1.1 Solder Bumping

Most chips are manufactured with peripheral bonding pads, while the highest density and performance redistribute the interconnects into an area array of solder bumps (Fig. 1).
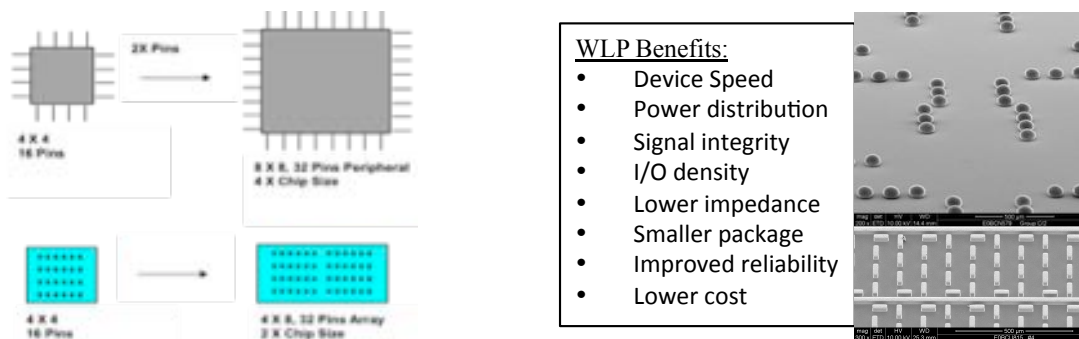

Fig. 1. Peripheral vs. orthogonal connections (left) with benefits & orthogonal bump array (right).

There are at least three methods of creating the solder bumps, including applying preformed solder balls, screen printing, and electroplating. Preformed solder balls are typically used for pad pitches greater than 200μm, while below this level,

* jmoore@daetec.com, (805) 484-5546, -56 Fax, www.daetec.com

screen printing and electroplating are dominant. Plating allows bumping at virtually any pitch that can be lithographically imaged. The sequence of wafer-level packaging with bumping is shown in Fig. 2.
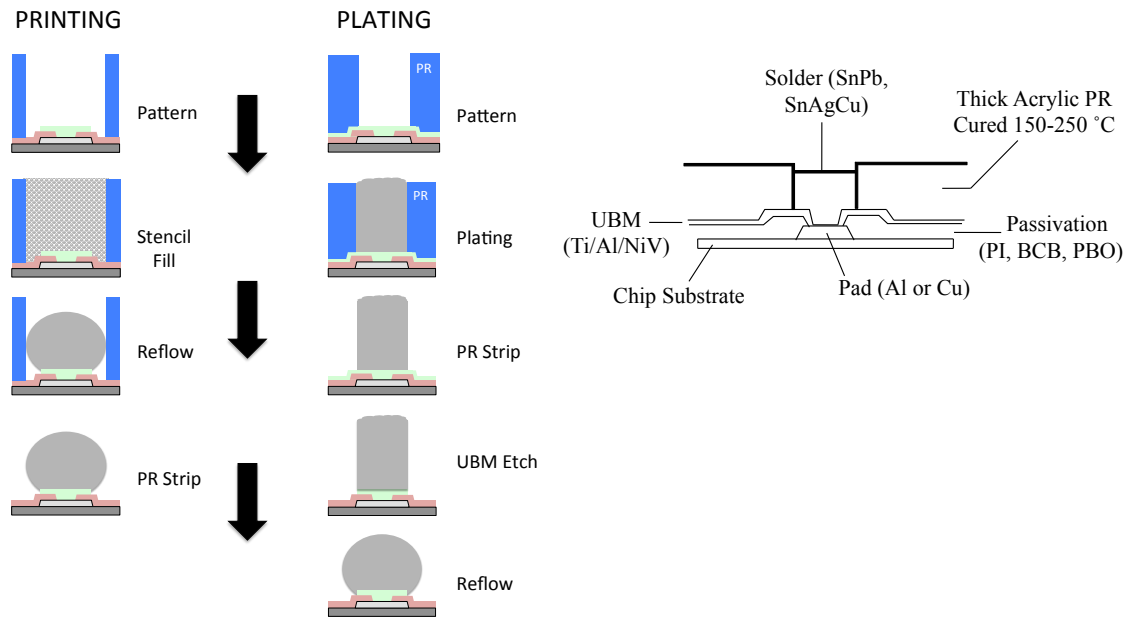

Fig. 2. Bumping process flow using printing and plating techniques (left) and plated bump circuit (right).

During an electroplating WLP process, under-bump pad is exposed by a via in a dielectric layer, followed by under-bump metallurgy (UBM) that provides a seed over a diffusion barrier and adhesion layer. The plating mask is formed by PR that may be 25-100μm thick. Following plating, the PR is stripped and exposed UBM is etched away. Prior to solder reflow to produce the smooth truncated spheres, bump appearance can vary from well defined, overplated mushroom shapes, to T-top formations (Fig. 3).

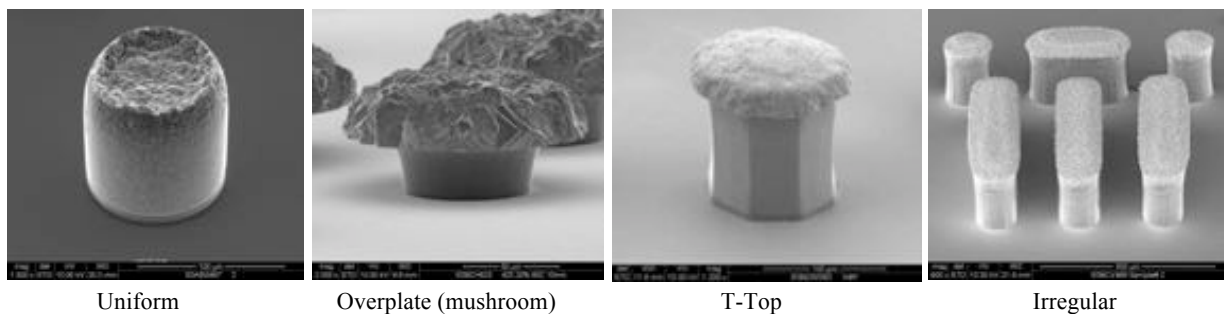Uniform   Overplate (mushroom)   T-Top   Irregular

Fig. 3. Bump shapes varying from uniform, overplated, T-top, or irregular.

Key yield parameters include co-planarity across the die and alloy composition. These are affected by seed layer, electrical contact, existence of "edge plating", cell symmetry, and the PR pattern. As the IC trend continues towards smaller sizes and lower cost, a greater need exists to increase the density of interconnections. To this end, tighter pitch and higher aspect ratio features are achieved with designs surrounding copper pillar technology.

Copper pillar configurations use the strength and rigidity of copper as a stand-off with the low melting wetting capactity of solder for bonding. While traditional solder and pillar plating can drive pitches to 150um, fine pitch pillars are targeting <50um. Copper pillars reduce the risk of shorts between adjacent bumps, facilitates larger spacing between

bumps for improved routing and flow of underfill, and offer a lower resistance as compared to pure solder. The use of pillar technologies will continue to drive packaging practices to tighter geometries which may demand higher resolution PR patterning considerations.
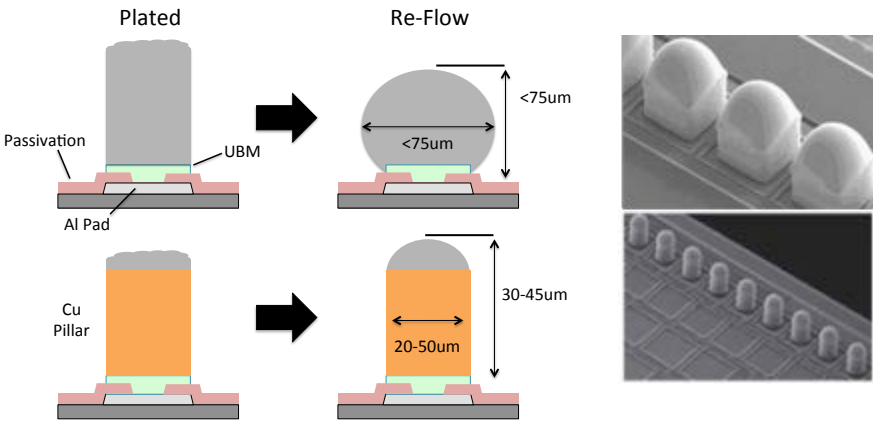

Fig. 4. Description of copper pillar design advantages (left) and reflow images (right, courtesy of Amkor).

1.2 Thick photoresist

Patterning is an integral part in WLP. The choice in PR is critical for technical and cost needs. Near vertical sidewalls are an important characteristic in defining the shape of the feature and ability to meet pitch designs [6]. While positive is used in bumping, negative is popular for thick coatings, resistant to reflow in printing and acid baths for plating. Acrylic resins are dominant in photopolymer PRs. An example is the free radical initiators that react with vinyl resins, propagating throughout the system to create a cross-linked polymer [4](Fig. 5).
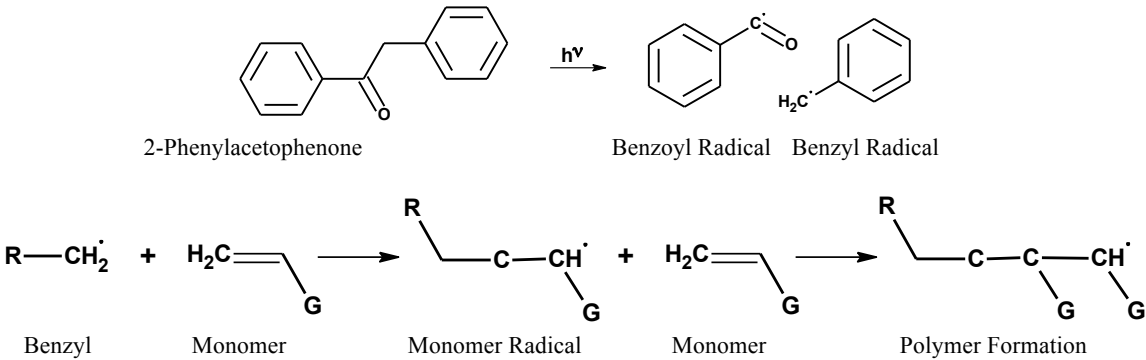

Figure 5. Radical generated photoscission (top) triggering resin chain polymerization (bottom).

Acrylic resists in liquid form are viscous with solids commonly >50% w/w. Solid form "dry-film" was designed to process circuit boards. Dry film PR is available in roll-form sandwiched between two sheets of plastic, polypropylene and polyester (mylar) (Fig. 6).
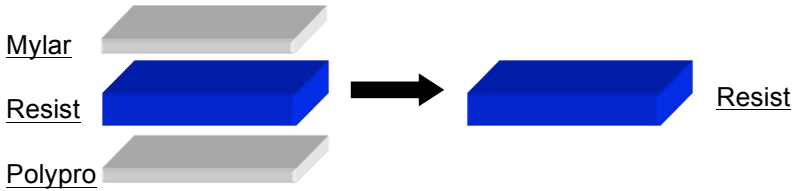

Fig. 6. Description of dry-film photoresist, sandwiched between two sheets of plastic.

When using dry-film, the polypropylene layer is peeled away to allow the resist to contact the substrate. Heat is applied and the photoresist fixes onto the surface. The mylar layer is retained on the surface during exposure and peeled away prior to development. Once developed, rinsed, dried and baked once again, the resist is ready for processing.

1.3 Photoresist stripping

The process of photoresist stripping is the simple removal of a resist species by a chemical. Negative-tone acrylics are cross-linked to form an impervious mask, and removal can present serious challenges. Commercial strippers are commonly based upon mixtures of organic solvents with aggressive alkali additives. The reactive chemistries break bonds and release monomers to the bulk medium, described by the following reaction (Fig. 7).

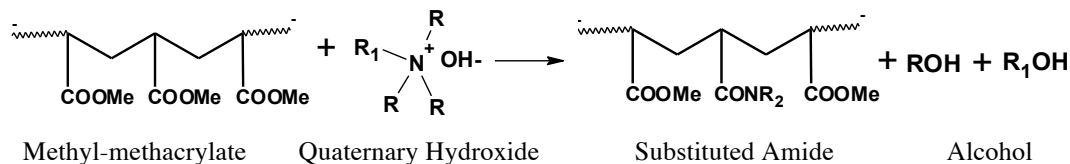| Methyl-methacrylate | Quaternary Hydroxide | Substituted Amide | Alcohol |

Figure 7. Breakdown of cross-linked acrylic by an alkali quaternary hydroxide (TMAH).

TMAH hydrolyzes bonds between methacrylate resins while the solvent penetrates. These pathways work together to swell and increase surface area for alkali action. Hydrolysis forms soluble amides that are rinsed by the solvent. This *infiltration model* describes how alkali and solvent work to break-up acrylic PR into small components that are filtered away. Without the aid of reactive materials, solvent penetration is non-existent or incomplete.

1.4 Aqueous performance

While positive-tone PR is dissolved by aqueous chemistry, negative PR is lifted-off from the substrate. Unlike organic solvents, aqueous systems do not swell the polymer. Instead, the chemistry travels at the interface between the PR and substrate, breaking bonds to release it and allow it to be sent to the bulk liquid where it can be filtered (Fig. 8).
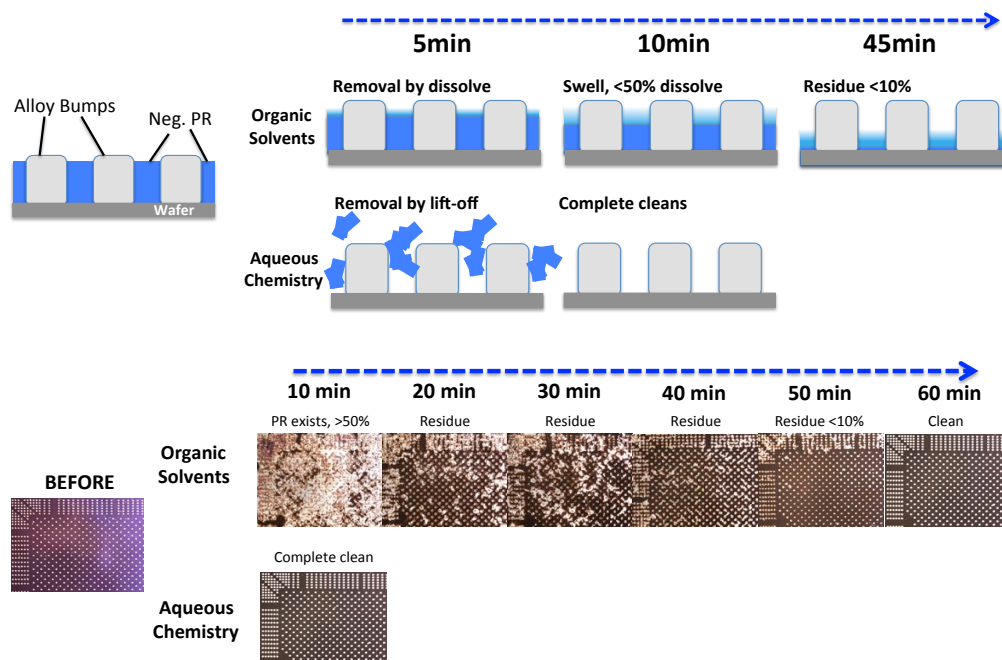

Figure 8. Neg. acrylic PR removal, solvents compared with aqueous (model – top, actual results – bottom).

Aqueous PR removal is conducted within minutes and filtered away from the wafer. Using a pore size of 100um or smaller in arrangements configured for easy PR separation, demonstrations occur whereby the cleaned wafer is produced along with the separated PR that once existed upon the substrate. Namely, the PR can be filtered, rinsed, and quantified as collected from the wafer (Fig. 9).
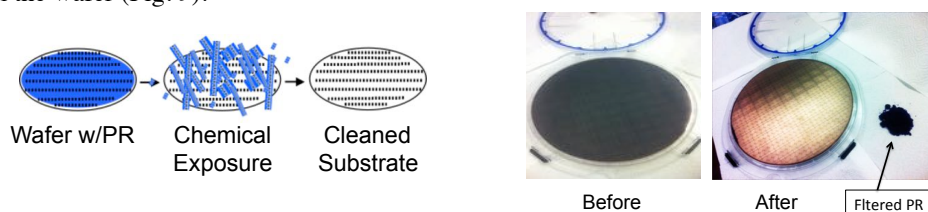

Figure 9. Aqueous removal of acrylic neg. tone PR, showing model (left) and actual (right) demo on a full wafer.

1.5 Corrosion protection

Inhibitors are required whenever aggressive chemistries are used in contact with sensitive metals. Choice depends upon solubility, pH, concentration, and performance. For example, benzotriazole (BTA) and tolyltriazole (TTA) are used for the adsorptive planar structure at <10Å in protecting Cu [7-8], while others operate as "lock-and-key" (aluminosilicates), complexing (phosphates), or chelation with molecular carbonyl character (citrates, pyrolles)(Fig. 10).
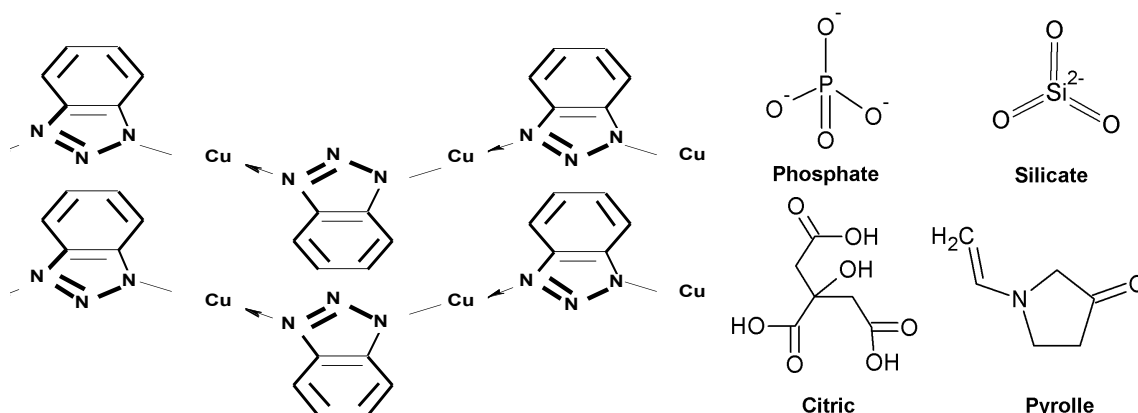

Figure 10. Planar structure in passivating Cu (left) and complexing Al and other transition metals (right).

Dissimilar metals in contact to each other can trigger galvanic corrosion. Strip chemistries can oxidize bump metal to produce Sn ions, which are reduced (plated) onto Cu UBM at the interface region. The phenomenon can be subtle, very thin (angstroms), and prior to UBM etch, is difficult to detect by OM or SEM. After UBM etch, irregular "Cu rings" exist at the base of the bumps (Fig. 11). Etch rate comparisons for various PR removal chemistries are given in Table 1.
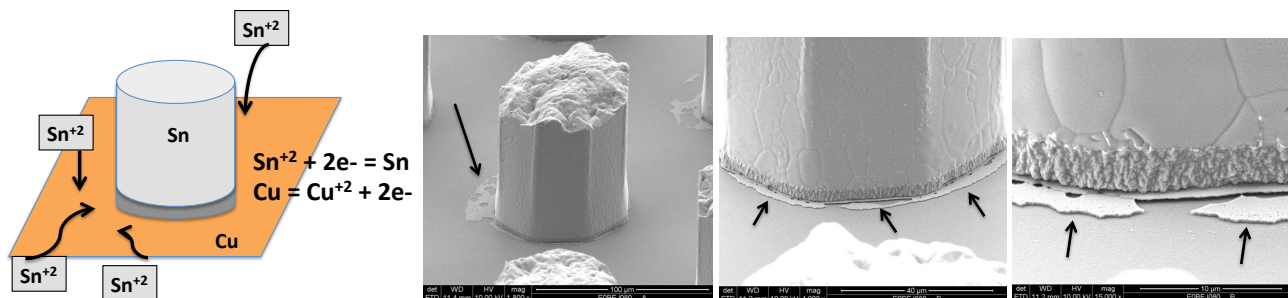

Figure 11. Galvanic corrosion produced by bump metal oxidation and subsequent reduction at the UBM interface (left). SEM images showing results of incomplete UBM etch originating from redox reactions at the interface (right).

Table 1. Etch rates of PR stripper chemistries, reported as Å/min.

Chemistry	Al	Cu	Ni	Sn	Pb	Ti
Alkaline Solvent	29	3	0	2	28	6
HA* Solvent	2769	30	1	27	124	4
Semi-Aqueous**	1060	6	0	17	17	6
Aqueous**	16	2	2	4	14	0
DIW	24	0	0	0	11	0

* HA = hydroxylamine solvent;   ** inhibited.

1.6 Bath Life

Bath life is defined as that amount of PR or number of wafers whereby continued processing in the chemistry no longer achieves the desired result. This number directly affects the cost of the process in bumping operations. Measurement occurs by PR loading and conversion to wafers per gallon (WPG). The process is defined by conditions.
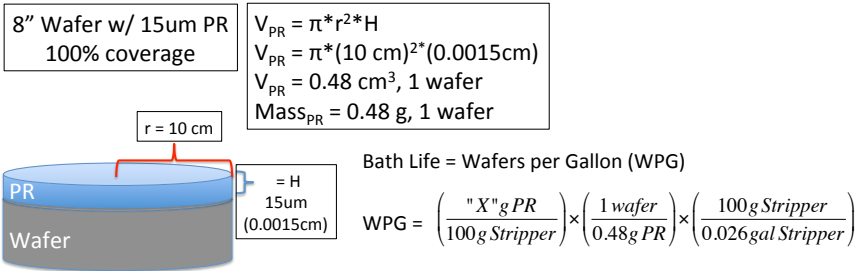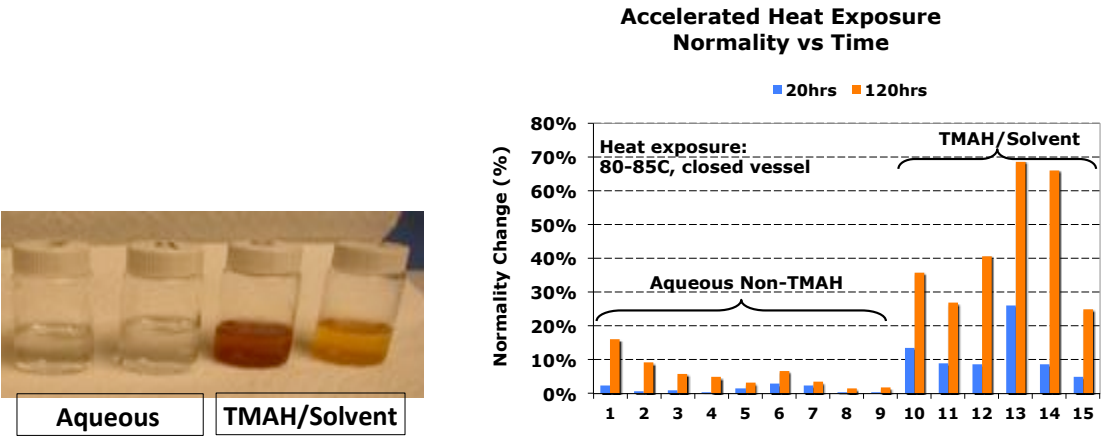
8" Wafer w/ 15um PR
100% coverage

$V_{PR} = \pi * r^2 * H$
$V_{PR} = \pi * (10 \text{ cm})^2 * (0.0015 \text{cm})$
$V_{PR} = 0.48 \text{ cm}^3$, 1 wafer
$Mass_{PR} = 0.48 \text{ g}$, 1 wafer

r = 10 cm

= H
15um
(0.0015cm)

PR

Wafer

Bath Life = Wafers per Gallon (WPG)

$$WPG = \left(\frac{"X" g\, PR}{100\, g\, Stripper} \right) \times \left(\frac{1\, wafer}{0.48\, g\, PR} \right) \times \left(\frac{100\, g\, Stripper}{0.026\, gal\, Stripper} \right)$$

Figure 12. Bath life calculations using common geometrical algorthms measured as wafers per gallon (WPG).

1.7 Stability

A reliable stripper chemistry will maintain its performance activity over time when held at a specific temperature. In the following example, various formulations representing non-TMAH aqueous based DaeClean[TM] strippers are compared with TMAH/solvent formulas held at 80-85C for up to 120hrs (5days). The aqueous non-TMAH chemistries exhibit highest solution stability as solution clarity and reduced normality change (Fig. 13).

Aqueous   TMAH/Solvent

Accelerated Heat Exposure
Normality vs Time

■ 20hrs ■ 120hrs

Heat exposure:
80-85C, closed vessel

TMAH/Solvent

Aqueous Non-TMAH

Normality Change (%)

Figure 13. Improved stability of aqueous-based non-TMAH PR stripper DaeClean[TM] vs. TMAH/solvent mixtures.

2. EXPERIMENTAL

2.1 Materials

Silicon wafers (1-0-0, ~525 µm) re-manufactured from Wollemi Technical, Inc. (Taiwan, www.wollemi.com.tw). PR's tested in these experiments include: AZEM P4620 positive-tone (www.emd-performance-materials.com, AZEM was acquired by Merck), negative liquid photopolymer PRs are provided as JSR THB-151N (www.jsrmicro.com), and BPR series (www.dow.com), negative dry-film varieties from the trade names Sunfort (www.asahi-kasei.co.jp), Riston (www.dupont.com), and TOK (www.tok.co.jp). Stripper chemistries include: DaeClean aqueous and non-aqueous products as described (www.daetec.com).

2.2 Equipment

Coatings are produced on a Brewer Science, Inc. CB-100 spin-coater. Imaging is produced on a Clearfield and SUSS MicroTec MA200 exposure machine with a 1000 W Hg arc lamp at varying intensities for pattern definition. Metal safety was done on an Ambios XP-2 surface profilometer with a 2.5um stylus. Analytical titer measurements were carried out with a Brinkmann autotitration system using 1.0N HCl in a Pt electrode for neutralization.

2.3 Methodology

PR patterned wafers were prepared by spin-coating or affixing negative dry-film by thermal bonding, PAB, and exposed and developed in TMAH (2.38%) to produce the desired patterns. Following mask definition, in-via solder studs on a Cu sputtered seed metal. These and other Pb-free bumping are plated and supplied for PR stripping (Table 2).

Table 2. List of substrates using thick photoresist manufactured from several suppliers.

Wafer ID	Wafer Diameter	Metal	PR Type	PR Supplier	PR Thickness
1	300 mm (12 inch)	Cu UBM	Pos. Liquid	Merck AZ P4620	50-60 um
2	200 mm (8 inch)	Cu UBM, Au Pads	Neg. Liquid	JSR THB-151N	20-24 um
3	300 mm (12 inch)	Cu UBM	Neg. Liquid	DOW BPR-100	50-60 um
4	150 mm (6 inch)	Cu UBM, Pillar	Neg. Dry Film	DuPont WB100 series	50-60 um, 100-120 um
5	300 mm (12 inch)	Cu UBM	Neg. Dry Film	TOK	50-60 um, 100-120 um
6	300 mm (12 inch)	Cu UBM	Neg. Dry Film	Asahi Sunfort	50-60 um

Coupons used for metal safety tests included copper plating on a seed (10,000 Å) and plasma deposited aluminum pads (10-12um). Immersion studies were conducted, rinsed in DIW, followed by IPA, and dried prior to OM, and Pt coating and Hitachi 4700 SEM analysis. Daetec's SOP #3, 10 & 18 were used for metal safety testing.

3. RESULTS

3.1 Performance

Wafers containing various resist patterns and topography were immersed and cleaned in DaeClean[TM] aqueous products, water and IPA rinsed, dried, and SEM analyzed. No corrosion is observed, performance in Table 3, SEM in Fig. 14.

Table 3. Results of performance testing for PR stripping using conventional solvents and aqueous on wafers described in Table 2.

| Wafer ID	PR Type	Thickness (um)	Solvent Removal (time & method)	Aqueous Removal (time & method)	Cu Etch (PPM) as solvent/aqueous	Notes
1	Positive	50-60	<15min, dissolve	<15min, dissolve	Clear/clear	none
2	Neg – liquid	20	30min, dissolve	<15min, lift-off	Clear/clear	none
3	Neg - DF	50-60	45min, dissolve	<15min, lift-off	Clear/clear	none
4	Neg - DF	100-120	45-60min, dissolve	<15min, lift-off	Clear/clear	none
5	Neg - DF	100-120	>60min, dissolve	<15min, lift-off	Not clear/clear	Solvent no cleans
6	Neg - DF	100-125	45-60min, dissolve	<15min, lift-off	Clear/clear	none
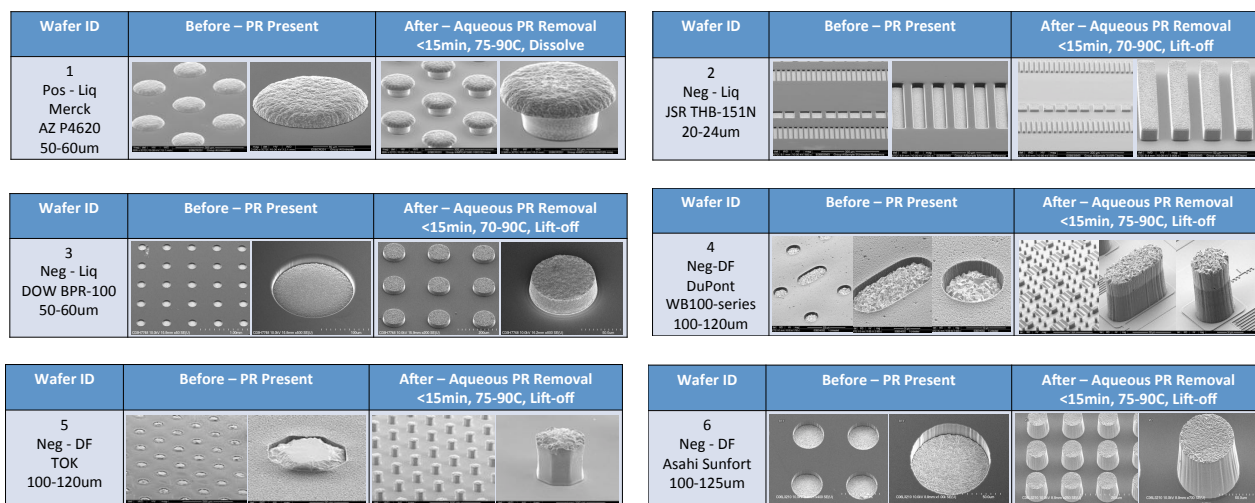
Figure 14. SEM photos of bumped wafers, before and after DaeClean[TM] aqueous stripping, 75C, 15min, DIW/IPA rinse.

3.2 Bath Life

Bath life taken to 5% w/w loading of PR conducted in DaeClean[TM] aqueous stripper and a conventional solvent system using positive PR (AZEM (Merck) P4620) and negative (JSR THB-151N). Removal results from substrates similar to those indicated in Fig. 14 using loaded stripper solutions tested at 75C for 15 min are given in Table 4. Bath life is the maximum PR loading level that achieves clean substrates for the given conditions (Fig. 15).

Table 4. Performance of loaded DaeClean[TM] and existing solvent solutions and representative bath life. For the examples stated, the positive PR bath life in solvent NMP is 2% w/w and aqueous is 3% w/w. Corresponding negative PR results are 1% and 4% for the solvent system (TMAH in DMSO) and aqueous-based DaeClean[TM], respectively.

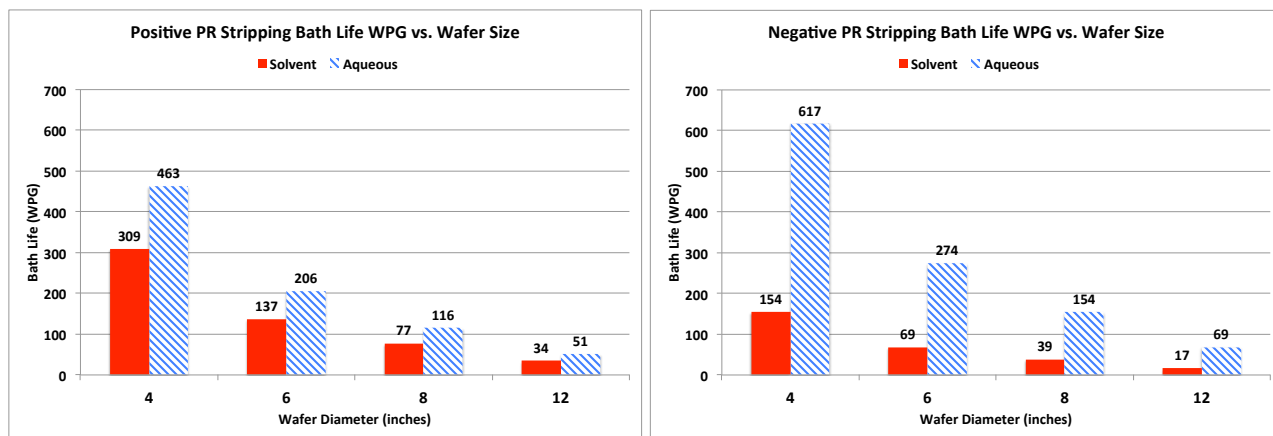| PR Type	Stripper	0	1	2	3	4	5
Positive	Solvent	Clean	Clean	Clean	Not Clean	Not Clean	Not Clean
	Aqueous	Clean	Clean	Clean	Not Clean	Not Clean	Not Clean
Negative	Solvent	Clean	Clean	Not Clean	Not Clean	Not Clean	Not Clean
	Aqueous	Clean	Clean	Clean	Clean	Clean	Not Clean

Figure 15. Bath fife (WPG) determination of positive PR (left) and negative PR (right) for solvent vs. aqueous DaeClean[TM] strippers. Wafers have ~20um thickness of PR with 100% coverage.

3.3 Analytical Monitoring

Aqueous DaeClean[TM] PR loaded chemistries are used to test various analytical parameters as pH and refractive index. Measurements over a range to 5% loading of positive PR is conducted (Fig. 16).
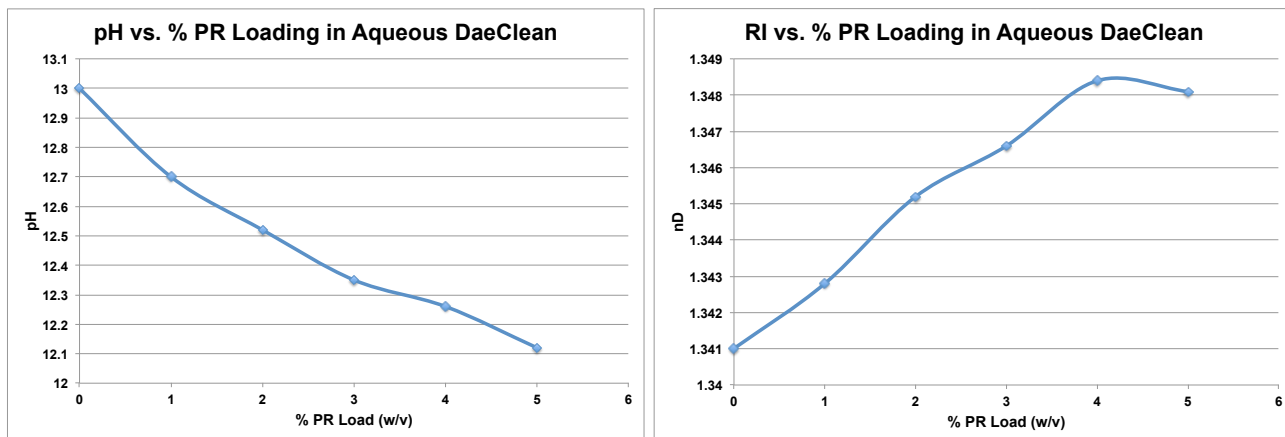

Figure 16. Measurement of pH (left) and refractive index (right) on aqueous DaeClean[TM] stripper solutions with positive PR loading.

4. DISCUSSION

Aqueous cleaning of PR is not a new concept. The use of cost effective solutions that reduce risk to the fab are under constant investigation. The performance of aqueous strippers is equal to or better than conventional organic solvents as explained by our modeling and testing (Secs. 1.4 & 3.1). Organic solvents cause swelling of the PR and prevent penetration to the substrate. While dissolving positive PR is similar between organic solvents and aqueous chemistries, negative PR exhibits crosslinked bonds that are broken consuming the bath chemistry. Due to the dissolution of negative PR, the organic solvent chemistry is depleted more than aqueous strippers, producing lower bath life values. Conversely, aqueous strippers lift-off PR from the substrate in record time where it is carried away and filtered off as trash. Reduced interaction from aqueous strippers will preserve the bath chemistry, producing a greater life.

One of the challenges in using aqueous chemistries is just that, the chemistry of water. Water has increased conductivity over that of organic solvents. When you compound that with chemistry, heat, and time, the chance for galvanic corrosion between dissimilar metals increases. The key example where this occurs is between the plated metal and the UBM as described earlier (Section 1.5). Aqueous DaeClean[TM] strippers use an inhibitor package that produces a phobic surface during stripping. During rinsing, the inhibitor is rinsed away to reveal an inert UBM surface, allowing it to be etched away with good clearing throughout. The use of aggressive sulfuric-peroxide mix (SPM) and phosphoric-peroxide mix (PPM) etchants both perform well in clearing Cu UBM during post stripping processing (Fig. 17).
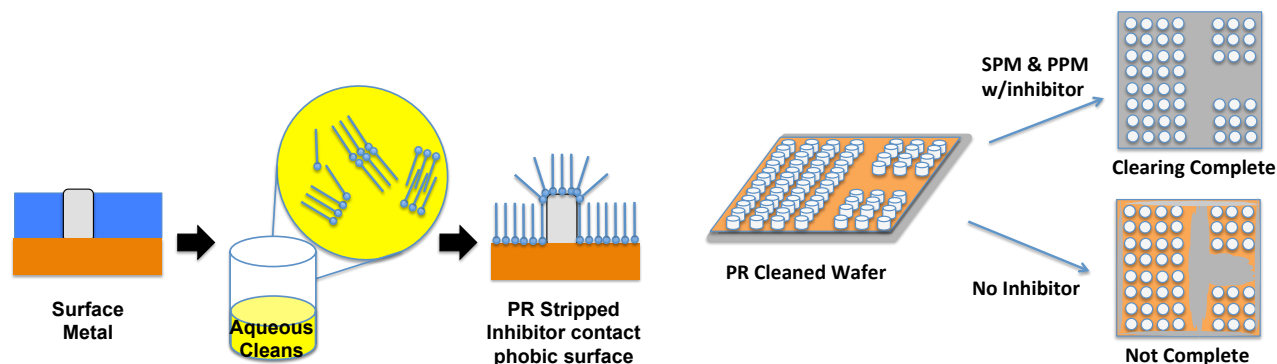

Fig. 17. Inhibitor package (left) in aqueous DaeClean[TM] stripper to allow post UBM etch processing to proceed (right).

5. CONCLUSIONS

WLP bumping processes are supported with aqueous DaeClean[TM] strippers to achieve high performance and bath lives that are 2-3X as compared to conventional solvent chemistries. Green products are shown to exhibit acceptable processing with lower cost. Integration into tooling is simple, using filtration technologies that are well established.

ACKNOWLEDGMENTS

The authors would like to thank our customers who submitted representative WLP bumped substrates to demonstrate the use of aqueous strippers in removing PR without challenge to key processing parameters.

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[9] DaeClean[TM] strippers are a trademarked product with Daetec (www.daetec.com).