

# Rapid and Controlled Stripping of Thick Resists for Semiconductor BEOL Applications

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## Abstract

Many BEOL semiconductor applications such as wafer level packaging (WLP) require thick photoresists commonly applied up to 100 $\mu$ m, to produce vertical wall patterns for densely populated electroplated structures such as in-via solder bumps.[1] Although negative-tone resists of the acrylic and acrylic-styrene resin varieties are common, their successful integration can depend upon the right choice in an aggressive stripper. This is due to severe chemical and thermal conditions, which enhance further curing. Key stripper chemistries containing high pKa value cyclic quaternary amines have been shown to work well to rapidly react with the residual acrylic acid character of the resin, hydrolyze, and free-up residual polymers. GenSolve™ 475, as produced by General Chemical,[2] achieves these goals to support cycling closed-loop spray processors, which filter and deliver the stripper back onto the wafer. When used at moderate temperatures in a spray tool, a wafer with a cured acrylic-polystyrene resist coated at >50 $\mu$ m will clear in seconds, be water rinsed, nitrogen spin-dried, resulting in a total process time under 30 minutes with a corresponding high throughput for a 300mm system. Using GenSolve™ 475 in a ZETA® Spray Processor, produced by FSI International, Inc.,[3] Pb metal alloy in-via bumps are proven to be free of residue and to have good surface integrity. High bath life is achieved by monitoring solution alkalinity titer and refractive index. Performance and metal safety is confirmed by SEM, and prior work with profilometry, ESCA, etch rates <30 Å/min, and top layer inhibition of copper.

## Introduction

Wafer level packaging (WLP) may be defined as rigid contact IC interconnects done at the wafer level. This back end of line (BEOL) processing takes the completed wafer and carries out etching and plating to install vias that connect each device on the front to a solder ball (bump) array on the back. The solder ball is typically attached to an electroplated under bump metal (UBM) or stud. The UBM provides the pad for attachment of the solder alloy that varies from copper, gold, and lead, to forms that include the shape of the conventional mushroom or the higher-density in-via type as shown in figure 1. Following reflow and wafer dicing, each chip is flipped over and thermally attached to a corresponding circuit board using the rigid bumps as contact, a process referred to as flip chip interconnect (FCI), a part of WLP. This eliminates the need for wires and conductive underfill, resulting in a reduction of size and cost.[1,4]

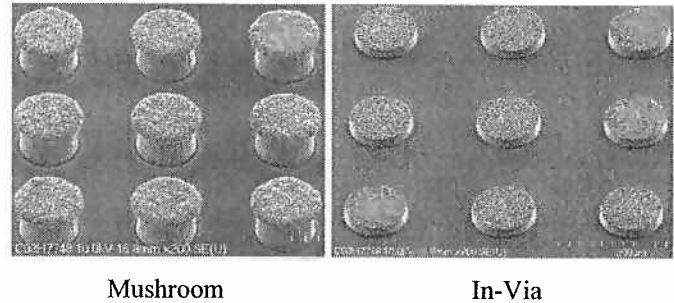


Figure 1. SEM photos of copper mushroom and in-via bumps.

The trend in miniaturization of IC manufacturing is supported by the in-via bump design where less solder is needed to complete the joint, resulting in a higher density array. Commonly, the bump is electroplated into high aspect ratio patterns as produced by thick negative-tone photoresists. The feature success is dependent upon the selective stripping of the resist to leave a clean metal surface that is free from defect and accepting of solder attachment.

## Thick Film Resist

It is well known that the use of negative-tone polymer platform systems, specifically from acrylate polymers, is suited for thick film ( $\geq 50 \mu\text{m}$ ) BEOL lithography applications. Near vertical sidewalls are important characteristics in defining the shape of the feature, especially for FCI structures.[5] Negative tone acrylic resists may involve a photochemically generated free-radical polymerization to cause linear and between-chain cross-linking (figure 2).

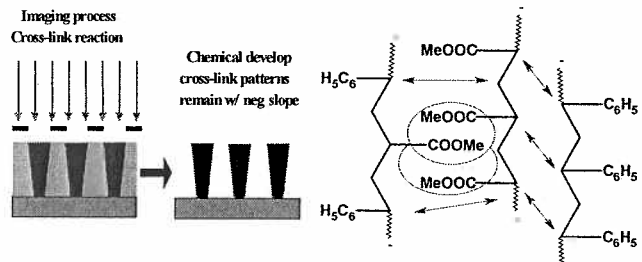


Figure 2. Exposure to produce linear and cross-linked chains.

Cross-linking is likely to occur when two or more monomers with vinyl character exist in the mix (i.e. methyl methacrylate, styrene, etc.). Homopolymerization and copolymerization promotes linearity, while cross-linking

between the chains may form at hindered locations where bulky side groups are present. Crosslinking enhances condensation to a denser and less soluble product. Many resist manufacturers formulate with different monomers to produce a material with unique properties of hardness, thermal and chemical resistance, and adhesion.[6]

### Photoresist Stripping

The process of photoresist stripping is the simple removal of a resist species by a chemical, commonly carried out in solvent systems. The ease by which a stripping process is done is enhanced by chemistries, which achieve selective dissolution of the unwanted polymer or residue while maintaining substrate integrity. When the unwanted species is dissolved, it is beneficial for a process as the mixture may be sent to a filter for cycling back through the system.

Dissolution of simple polymers (i.e. thermoplastics) involves a polarity-driven “likes dissolve likes” interaction, where the character of a solvent is matched with that of the solute. An example is the *infiltration* model, where solvent molecules dissolve a polymer through penetration, infiltration, gel-formation, and finally, break-up and transport to the bulk media where it repeats until dispersion is complete.[7]

When the solute is crosslinked, reactive chemistries must be used in the stripper. Without the aid of reactive materials, solvent penetration is limited and the process of dissolution is inhibited. Reactive materials include acid/base, complexing, and redox (reduction-oxidation) agents, which work with the solvent concurrently, to react and dissolve the solute. For example, an acrylic resist may be more easily attacked and dissolved away by attacking and neutralizing the residual acid character of the resin with an organic alkali (Figure 3).

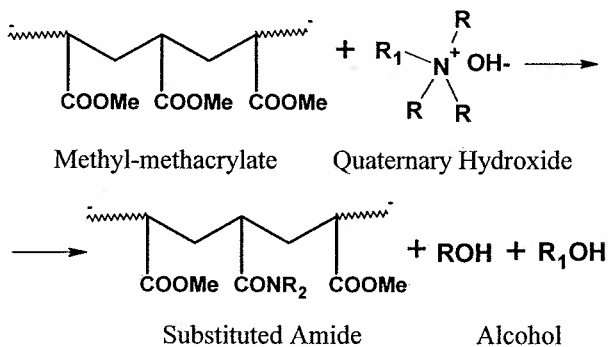


Figure 3. Organo-alkali Reaction with Acrylic Polymer.

In this case, the alkali (quaternary amine-hydroxide) reacts with the residual acrylic acid (methacrylate) of the resin to hydrolyze (break bonds) the molecule while the solvent assists in penetrating the overall system. They work together so that as the swelling occurs, more surface area is exposed for action by the alkali, and vice-versa. The result is continued hydrolysis of the methacrylate polymer to form more soluble

amides, cleaving the polymer string, and ultimately resulting in simple molecules that are completely dissolved.

A preferred stripper chemistry for stripping acrylic negative-tone photoresists is GenSolve™ 475. This patent-pending product contains a strong (high pKa) cyclic quaternary amine-hydroxide, designed for breaking bonds in highly cured polymeric systems.[8] Processing applications where resist thickness approaches 100um suggests that GenSolve™ 475 will maintain performance.[9]

### Residue Removal in Automated Batch Spray Tool

Residue removal for BEOL applications requires automated tools to be very versatile in terms of the chemical compatibility of the materials of construction, process temperatures and chemical dispense times. Figure 4 shows a schematic diagram of the spray processor used in this study, the FSI International ZETA® Surface Conditioning System. This system is a batch spray processor that utilizes centrifugal force for enhanced particle removal and drying. The process chemistry can be dispensed via center and side spray posts from a fresh or recirculated source, depending on chemical cost and dispense time.

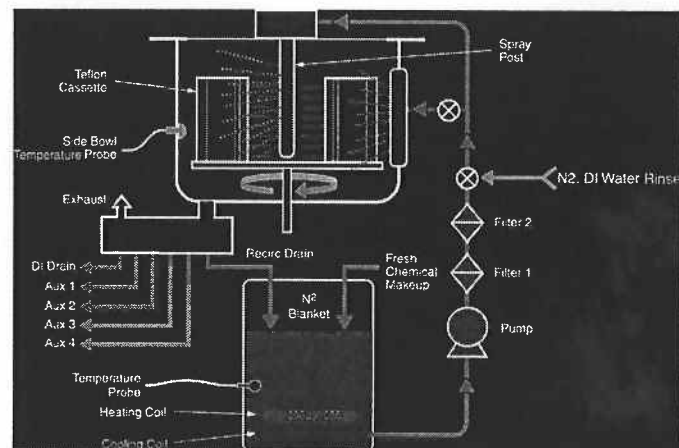


Figure 4. ZETA® Surface Conditioning System.

Bath lifetime is often critical in minimizing the cost-of-ownership. In addition, BEOL chemistries are often sensitive to oxidation at operating temperatures. Therefore, the system described herein, utilizes a nitrogen atmosphere for both the process chamber and chemical storage tanks to minimize chemical degradation. Chemical rinsing is often critical to reduce metallic corrosion, which may occur if removal chemistries remain on the wafer during exposure to ambient conditions. The rinsing system shown in Figure 4 is designed such that the center spray post rinses the wafers while, the side spray posts are primarily designed to rinse the wafer cassette and rotating turntable. Finally, the process temperature is very important in controlling film loss and maintaining a high selectivity between the residue and substrate. In general, film

loss increases and selectivity decreases as the temperature is increased outside the recommended temperature range.

### Experimental

Photoresist and patterned wafers were supplied by JSR Corporation (Japan).[10] JSR supplied 200 mm wafers coated with approximately 80um of negative acting THB-151N resist, with in-via solder bumps on a sputtered seed metal Cr/Cu (50/150nm) film. The wafers were then spin coated, PAB, and exposed to 1000-1100 mJ/cm<sup>2</sup> of radiation @ 420nm and developed in TMAH (2.38%) to produce approximately 140um diameter hole size patterns. The plated bumps are Pb/Sn (95/5) of a height at 70um.

Coupons used for metal safety tests included copper plating on a seed (10,000 Å) and plasma deposited aluminum pads (10-12um). For the evaluation in the spray tool, a FSI (50 wafer) batch tool was used with Gensolve™ 475 using a pre-heated chamber temperature set to 80C. All specimens were Pt coated and analyzed by a Hitachi 4700 SEM, or similar. Metal safety evaluation was done on an Ambios XP-2 surface measurement instrument with a 2.5um stylus. Electron spectroscopy for chemical analysis/x-ray photoelectron spectroscopy (ESCA/XPS) with a Physical Electronics Quantum 2000. Analytical titer measurements were carried out with a Brinkmann autotitration system using 1.0N HCl in a Pt electrode monitoring electrolyte for neutralization.

Monitoring the reactive performance level in the resist stripper was modeled indirectly by measuring alkalinity with a wet chemical autotiter method. Samples of the JSR resist were blanket coated on Si wafers and cured by UV exposure and high temperature bake-out. The blanket coats were scraped from the Si wafer surfaces, broken-up into flakes and redissolved in NMP. Samples of the resist solutions are then mixed with various quantities of GenSolve™ 475 at elevated temperature for a period not exceeding 30min and then the remaining solutions are tested for alkalinity. This method was used to demonstrate potential bath life of the chemistry over time as resist loading occurs.

### Results and Discussion

Bath life measurements were carried-out with an autotitrator method for alkalinity. When testing a standard volume of GenSolve™ 475 as a baseline, the result indicated a titer value of 3.850 equivalents (eq) at the endpoint (EP). Using the same approach, titer measurements were conducted on given quantities of dissolved resist exposed to GenSolve™ 475 and the remaining alkalinity measured as a titer value. The figures 5 & 6 show a standard reference graph of the titer value of GenSolve™ 475 and the resulting titer results as resist loading occurs, respectively.

Performance of GenSolve 475 Stripper Measured as Alkalinity Titer

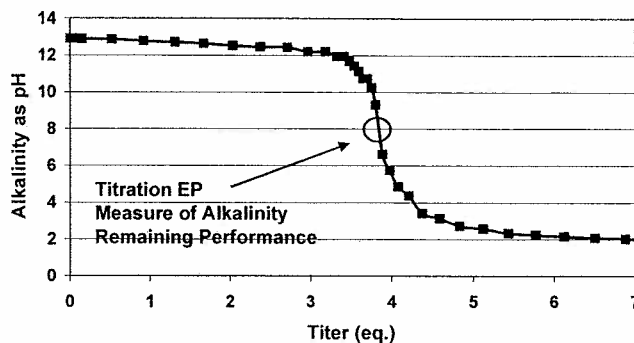


Figure 5. Titer value measured on GenSolve™ 475.

Performance of GenSolve 475 Stripper Titer Change with Resist Loading

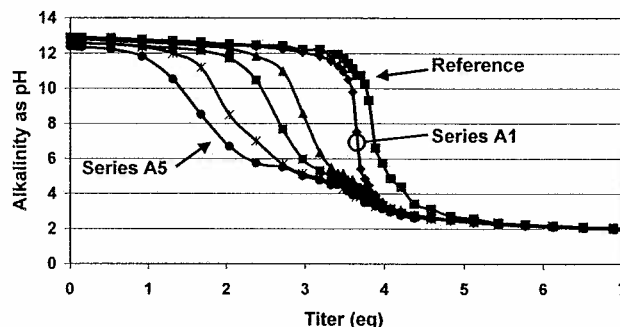


Figure 6. Titer value measured on GenSolve™ 475.

The measured values of each titer determination and refractive index vs resist loading are given in table 1.

Table 1. Changes in GenSolve™ 475 titer and RI with JSR resist loading. Values are calculated for a 5gal bath.

#	Loading (%)	Titer (eq)	Refractive Index
Ref	0	3.850	1.4655
A1	0.475	3.647	1.4653
A2	1.426	2.925	1.4661
A3	2.376	2.484	1.4665
A4	3.320	1.903	1.4670
A5	4.750	1.411	1.4676

The values in table 1 are graphed to determine the estimated bath life of a 5gal tank of GenSolve™ 475. When graphing this data, one can use it to predict bath life, using a monitor for titer reduction vs bath loading (figure7).

