An Evaluation of Bath Life Effects on Photoresist Removal for Wafer Level Packaging

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Abstract

With the emergence of 3D integration and wafer level packaging, the pillar bumping process has become a critical processing step. As the process has matured, significant efforts have been made for optimization in terms of both production and cost. This is especially true for photoresist stripping, since thick photoresists are needed to pattern high aspect ratios and must be removed in subsequent steps to expose underlying metal films. In this study, the removal of a thick negative tone photoresist with solder pillar plated wafers were investigated using a dimethyl sulfoxide blend with a quaternary ammonium hydroxide. Emphasis was placed on exploring the feasibility of an extended bath life beyond 7 days. Coupon level beaker tests were used to provide insight into the swelling and dissolution mechanisms with fresh and aged chemistry. Additionally, several chemistries were compared to examine the effect of the quaternary ammonium hydroxide. Based on these findings, chemical aging studies were performed on 300 mm wafers using a highly customizable single wafer processing tool that combined soaking and a high-pressure spray processing to potentially prolong the bath age even further. In addition to stripping efficiency at extended bath life, the compatibly with pillar structures and seed layers is investigated. Results from the study highlight potential methods to extend bath life while maintaining photoresist stripping efficiency.

Key words

Negative tone photoresist, bath life, photoresist removal, wafer level packaging, single wafer processing

I. Introduction

As additional and more complex steps are introduced in wafer level packaging (WLP) it has become critical to examine means to reduce costs. A common source of expense is chemical exposure and usage during wafer cleaning, which can account for over 50% of semiconductor processing steps [1]. Specifically, photoresist removal had a market valued at ~450 million USD in 2010 and would be expected to be significantly higher today [2]. Therefore, developing methods to extend the usage and effectiveness of stripping solvents has become a topic of increased interest.

For far-back end of line (FBEOL), negative tone photoresists have become prevalent as solder and copper pillar bump processing require thick resists layers (> 50 μm). Beyond being able to be spun on in thick layer, negative toned resists also show improved sidewall profile, reflow resistance in printing and acid baths, and are typically more cost-effective than positive resists [3, 4]. However, to achieve many of these characteristics, cross-linking of the resist is necessary, which can form an impervious mask that causes issues with efficient stripping [5-7]. The most common stripping deficiencies seen with negative toned photoresists are residues around the collar of pillar structures, incomplete removal in densely packed regions, and visibly undetectable films that inhibit under-bump metallization (UBM) etching [6, 8-10]. Ultimately, failure to completely strip a photoresist can result in contamination, metal residues, yield loss, and downstream complications.

Thus, it is necessary to select an appropriate stripping solvent that will ensure complete photoresist removal. However, several factors such as material compatibility and cost are also essential. Bath life is a main concern for many solvents, which is both a function of temperature and quantity of wafers processed. Prolonged exposure to elevated temperatures can decompose chemicals in the solvent leading to undesired effects such as corrosion of the pillar structure or seed layers [11-13]. Avoiding these adverse effects requires frequent replenishment of stripping solvent that can drastically increase process costs.

In addition to chemistry, the method of removal can also have an impact on stripping capabilities and bath life [10, 11, 14]. Leveraging the appropriate chemistry with process requires an understanding of the stripping mechanisms. Thus, in this study, comprehensive beaker level tests were conducted using a dimethyl sulfoxide (DMSO)-based solvent with a non-TMAH quaternary ammonium hydroxide (Chemistry A) to strip a negative tone photoresist. The technical data sheet for Chemistry A recommends a maximum bath age of 3-days. Insights gained from investigating stripping mechanisms and bath age were implemented in a single wafer tool to process 300 mm wafers containing electroplated solder pillar structures, which enables a robust process in high volume manufacturing. These initial results provide a basis to further develop methods to improve bath life.

II. Experimental

Studies were performed with two different wafer types: (i) 300 mm blanket wafers which were patterned, exposed, and developed and (ii) 300 mm solder pillar plated short loop wafers. The blanket wafers (i) were cleaved into 4 cm x 2.5 cm coupons and used for beaker testing, where half of the of the sample was immersed in 400 ml of solvent heated to 70°C +_0.1°C. After stripping, rinsing was performed in a separate beaker containing DI and were dried with N_2. Plated wafers (ii) were processed on a Veeco WaferStorm® wet processing system using ImmJET™ batch immersion and single wafer spray technology. The immersion station holds approximately 6 gallons of chemistry that is recirculated using a pump and passes through a filter and heater. Solvent is also held in tandem pressurized vessels, which passed through two-stage filtration, a high-pressure chemical (HPC) pump, a heater, and is delivered to the processing chamber. During dispensing, solvent was collected that was further recirculated through the tool. After the 300 mm wafers were soaked and sprayed, wafers were rinsed and spun dry.

III. Results and Discussion

A. Beaker Tests

Negative tone resists have proven challenging to strip, mainly as cross-linking prevents effective dissolution. Undissolved resist increases potential for higher defectivity levels, higher chemical consumption, shorter bath life and filter lifetime [15]. Undissolved resist often swells and lifts off the wafer into the bulk solvent, resulting in large residues that can clog filters, chemical lines, or nozzles. While tools with proper filtration can mitigate this issue, there is still potential for residues to redeposit onto the wafer surface [10]. As a result, it is preferred to select a solvent that can properly dissolve the resist. As the list of resist and solvents continues to expand, it becomes more important to understand the stripping mechanisms of resist and solvent pairing. N-methyl-2-pyrrolidone (NMP) is a common solvent for stripping applications, but often requires the incorporation of TMAH for dissolution of thick negative toned resists [9]. In general, there is a growing trend to move away from NMP due to environmental concerns and employee safety, so it is important to explore different chemistries [9, 14]. Therefore, this study examines the effectiveness of Chemistry A, a DMSO based solvent with a non-TMAH quaternary ammonium hydroxide. Chemistry A is compared to DMSO and NMP in removing a 75 μm negative photoresist on patterned, exposed, and developed blanket wafers. By comparing Chemistry A with these two solvents, the stripping mechanisms, and the significance of the quaternary ammonium hydroxide could also be properly assessed.

Wafer coupons were immersed in respective solvents for 30 min at 70°C. In all cases, the photoresist was seen to swell and lift-off from the substrate, but dissolution was only apparent using Chemistry A. After the 30-minute test, the lifted residue was no longer visible, whereas large residue could still be seen suspended in the DMSO and NMP solvents. Fig. 1 shows the surfaces of the coupons after completion of the beaker tests, highlighting a completely stripped surface using Chemistry A. Profilometry also shows a relatively flat surface and has the lowest contact angle (44°) of the three samples indicating complete removal of any photoresist. Samples soaked in DMSO and NMP show a clear residual film that was accentuated by the exposed pattern. Profilometry measurements across the patterned area reveal a step height of ~15 nm for DMSO and ~20 nm for NMP. Combined with contact angle measurements, results indicate that DMSO is slightly more effective in stripping the negative toned resists than NMP. While the residual film for DMSO and NMP processed coupons is relatively thin, it could significantly inhibit subsequent under bump metal etching steps.
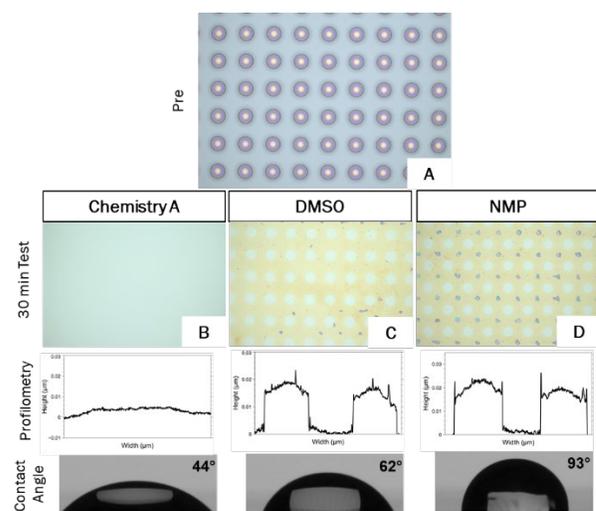
Figure 1: A) optical image of patterned blanket wafer. Optical images, profilometry scans, and contact angle measurements post B) Chemistry A, C) DMSO and D) NMP tests.

These findings highlight the effectiveness of the quaternary ammonium hydroxide contained in Chemistry A. TMAH has been shown to hydrolyze the cross-linked bonds into dissolvable pieces while the solvent penetrates the polymer. This leads to a combined mechanism of swelling and dissolving of the resist [5, 11]. Thus, the dissolution observed in the beaker tests reveal that the quaternary compound in Chemistry A is inducing similar effects. Based on the results from DMSO and NMP, swelling and lift-off of the resist is complete but the driving force for dissolution is necessary to remove the remaining residual film.

Since it was demonstrated that Chemistry A could effectively dissolve and strip the resist, the next step was to further understand the swelling and dissolution mechanisms. Beaker level tests with coupons performed in interval of 60, 90, 120, 300, 600, and 1200 seconds were performed in Chemistry A at 70°C (Fig. 2). The results from these tests show that penetration of the solvent occurs around 60s (Fig. 2B) and swelling initiates from the patterned areas leading to wrinkling of the film at 90 seconds (Fig. 2C). 30 seconds later, the bulk resist is carried away into the bulk solvent medium, leaving behind a thin residual film similar to what was observed for DMSO and NMP tests (Fig. 2D). Profilometry measurements recorded an average step height of 15 nm across the patterned and non-patterned regions, similar in thickness to the other solvents. This thin layer is slowly dissolved and completely removed by 300s, where the microscopy image displays a residue free film (Fig. 2E).
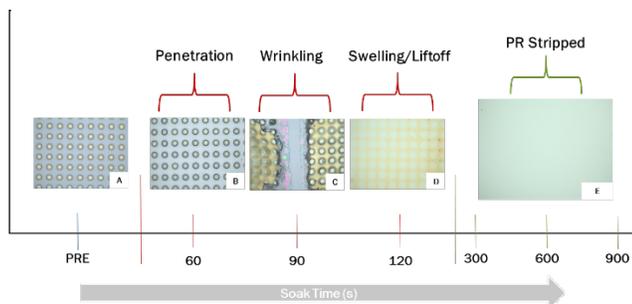
Figure 2: Opitcal microscopy images of coupon wafer surfaces after immersion in Chemistry A for select times A) 0s, B) 60s, C) 90s, D) 120s, and E) representative image of coupons tests between 300- 900s.

Initial data demonstrates that Chemistry A can readily dissolve and strip the negative toned resist using fresh chemistry, however it is not cost effective to continuously replenish new chemistry for a process. Thus, bath life becomes an important concern for customers in reducing cost of ownership. One factor to consider is bath lifetime at operation temperature. To simulate this, coupons were immersed in Chemistry A for 30 minutes at 70°C up until 15 days. Contact angle measurements were performed once tests were completed to compare removal efficiency.

Fig. 3 presents the findings from the bath life experiments, where incomplete removal is observed at 7 days. For tests up to 5 days, optical microscopy shows a residue free surface and contact angle measurements reveal comparable surface quality. Beyond 7 days, the bulk photoresist swells and is lifted off the substrate but a similar residual film observed in previous beaker tests is left behind. Furthermore, the photoresist did not fully dissolve during the 30 min experiment time, as exhibited with tests before 5 days. The ineffectiveness of Chemistry A in stripping the negative toned resists at the extended bath life was attributed to the consumption or the decomposition of the quaternary ammonium hydroxide at elevated temperatures. The thickness of the remaining film is consistently recorded at ~20 nm, suggesting that the rate of dissolution is significantly decreased, and this layer cannot be removed without an additional driving force (i.e. chemical or physical). Despite the inability for complete stripping of the resist, the bulk of the photoresist was still lifted off even after a 15-day aged bath.
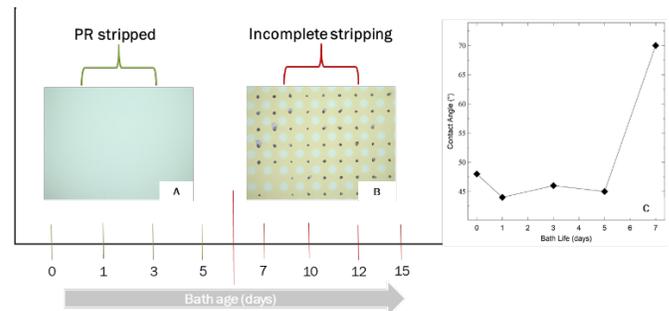
Figure 3: Optical imags of coupon surfaces post bath age studies displays representative images for A) 0-7 days and B) 7-15 day tests. C) Contact angle measurements results.

B. WaferStorm® System Configuration – 300mm wafers

While beaker tests with blanket photoresist wafers displayed effective removal after 5-day soak life, it should be mentioned that removal behavior of photoresist can be geometry dependent, where areas with dense pillar structures can prevent penetration of the solvent, limiting effective swelling and dissolution of the photoresists [5]. Many studies have explored agitation in the forms of ultrasonics, mixings, and sprays [10, 14-16]. Besides the intrinsic effects in improving stripping efficiency, agitation techniques provide potential to increase bath life [11]. Therefore, combining a soak process, as experimented in the beaker tests, with an agitation technology could prolong the chemical usage.

This dual step process was explored on solder plated 300mm wafers using a Veeco WaferStorm® tool with ImmJET™ technology that combines batch immersion and single wafer high-pressure spray. The tool was loaded with Chemistry A, and wafers were soaked in a heated and recirculating solvent bath for 30 minutes. Following the soak, the wafer is

transferred wet with a meniscus of solvent to a single wafer spin process station where a 60s HPC fan spray provides mechanical agitation to enhance residual removal. A schematic of this process can be seen Fig. 4. A final spin rinse and dry (SRD) step is performed with DI and IPA to ensure a clean wafer. Soak and HPC spray times were selected to ensure optimal cleaning of the wafer structures even at an extended bath life.
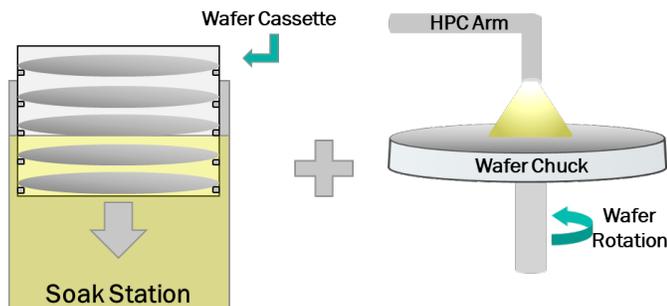
Figure 4: Schematic of Veeco's ImmJET™ technology which combines bath immersion and single wafer high pressure chemical (HPC) spray for resist removal.

C. Day 0 Chemistry: 300mm

With a 0-day bath life of Chemistry A, complete removal of the bulk resist with no indication of residues on the surfaces is exhibited (Fig. 5). In addition to stripping efficiency, attack of the solder pillar and copper seed needs to be controlled as to not impact subsequent UBM etch processes. Quaternary ammonium hydroxides can be aggressive on solder bumps so examination of the pillar structure will be critical for assessing Chemistry A [12]. Based on SEM imaging, no apparent attack to the pillars was observed. Even with the added intricacy of the pillar structures, the experimental setup with Chemistry A was able to completely strip the photoresist and exhibited minimal effects in terms of metal compatibility.
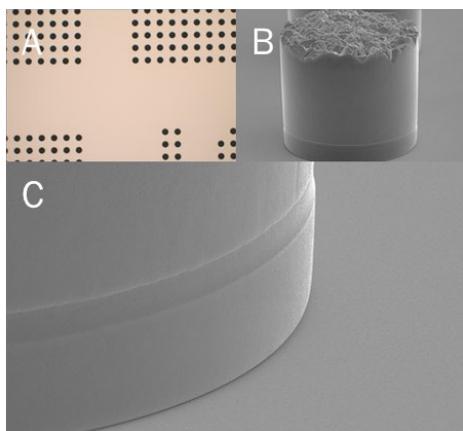
Figure 5: A) optical image and SEM image of B) entire pillar and C) base of pillar after being processed with fresh (0-day) chemistry.

D. Day 7 Chemistry: 300mm

With a bath life of 7 days, optical images of the wafer reveal increased staining at the edges of the channels as seen in Fig. 6A (red arrows). SEM reveals that staining is induced by nanosized pitting, where darker stained areas were correlated to larger and more dense pitting. While not completely understood, it is possible that the pillar patterns are generating a variable wetting behavior during processing leading to pitting in select regions. Similar behavior has been documented for copper PVD films in the presence of TMAH [17]. Overall, the pitting was limited to the nanoscale and no evident attack on the pillar was observed. While not shown in this study, EDS did not indicate any apparent oxidation of the copper seed layer and undercut was not detectable with cross-section SEM.
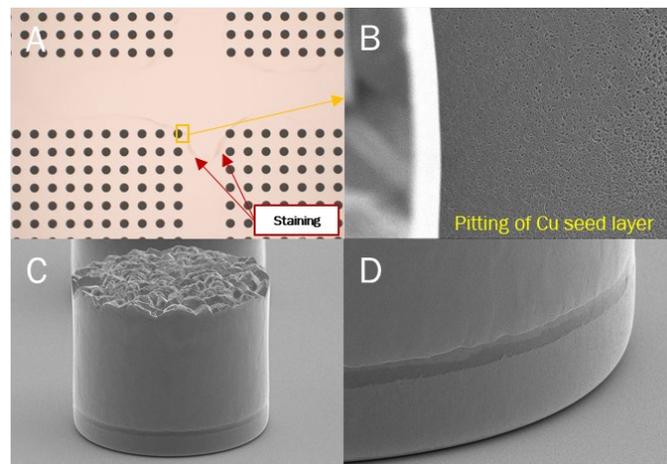
Figure 6: A) optical image of wafer surface and SEM image images of B) Cu seed layer, C) entire pillar and D) base of pillar after being processed with 7-day aged Chemistry A.

To ensure that the pitting of the copper seed layer would have no effect on the UBM etching steps, a coupon was cleaved and immersed in 1:1:100 mixture of H_2SO_4: H_2O_2:H_2O for 45s to etch the copper seed layer. The copper seed layer was removed (Fig. 7) and there were no signs of pitting in the underlying Ti layer.
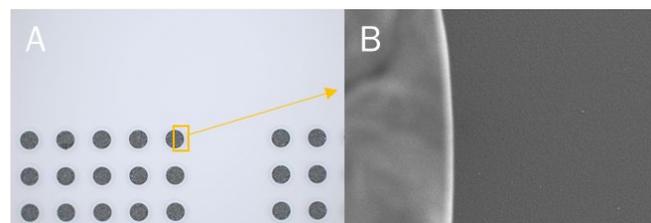
Figure 7: A) optical image and B) SEM image of 7-day aged processed wafer post Cu seed layer etch.

Through a combination of a soak and spray process, the bath life of Chemistry A was extended to a minimum of 7 days.

Compared to the beaker level tests on blanket wafers, this was at maximum, 48 hrs beyond expectation with a soak only process, and the lack of pillar structures likely led to an overestimation of the bath age performance. A test conducted with a commercial photoresist stripper with TMAH showed residue remained on pillar plated wafer after being processed with 48-hour aged chemistry [18]. Thus, it is evident that the HPC spray is playing a significant role in extending the process window of the aged chemistry.

E. *Day 14 Chemistry: 300mm*

To push the process window out further, a wafer was processed with a 14-day bath life. These wafers had significant amounts of residual photoresist, resulting in a swirl like pattern, where the center of the wafer appears to be effectively stripped. Haze maps have been shown to be a reliable way to detect photoresists as it generates a detectable fluorescence signal [19]. A haze map (Fig. 8A) was able to reliably detect the bulk photoresist that was remaining on the wafer. Through contrast detection, it was possible to determine the remaining area percent of residual photoresist. At roughly 65% photoresist remaining on the wafer, there is a significant drop off in stripping efficiency from the 7-day results.

From the optical microscopy image in Fig. 8B, the bulk residues have been localized to the dense structured regions of the wafer. The channels remain clear of photoresist, but discoloration of the copper seed layer is significant, indicating increased pitting. Utilizing the same copper etch as performed for the Day 7 tests, complete removal of the seed layer (Fig. 8C) was achieved, indicating that even with more severe pitting, there are no adverse effects on the UBM etch steps.
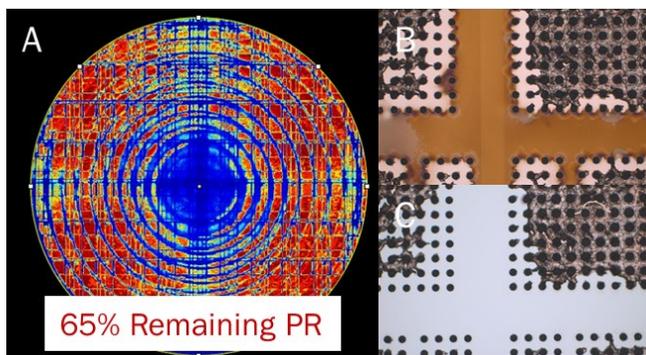
Figure 8: A) haze map and optical images of B) wafer after processing with 14-day aged Chemistry A and C) post Cu seed layer etch.

Photoresist residue also remained on the pillars in the form of full sidewall coverage residue (Fig. 9A) and collar residue (Fig. 9B). The collar residue has been mentioned in other works and either additional solvent exposure or further agitation is necessary to remove [10]. Despite the residue and

the pitting observed on the copper seed layer, there is no obvious impact to the pillar structure with a 14-day aged solvent. A similar 14-day wafer was re-processed in the same bath and the bulk photoresist residue appeared to be removed. It is therefore possible to further optimize the process through an extended HPC spray that could remove the remaining residues.
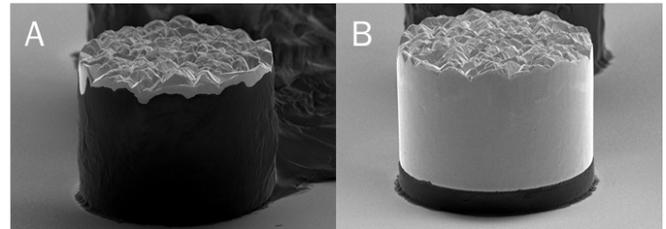
Figure 9: SEM images showing types of residues on pillar structure, A) full sidewall coverage and B) collar residue after being processed with 14-day aged chemistry.

III. Conclusion

This study provides a comprehensive examination of Chemistry A in stripping a thick negative tone photoresist for advanced wafer packaging applications, while exhibiting acceptable material compatibility with the pillars and seed layers. Successful stripping using 7-day aged chemistry was demonstrated, with a process window between 7 and 14 days using this standard process. Results from the 14-day bath age tests provide promise that bath age could be extended with further process optimization, however, severe pitting of the copper seed layer needs to be monitored. The ability to remove and dissolve the resist was shown to be heavily dependent on the reactivity of the quaternary ammonium hydroxide, which degrades at a longer bath age. However, utilization of the HPC spray appears to assist with dissolution and photoresist stripping by extending the useable bath age of Chemistry A to 7 days for pillar plated 300 mm wafers, which is 4 days longer than the recommended bath age by the supplier. In future studies, bath life factors such as photoresist loading will also be investigated, in additional to possible "spiking" schemes to replenish the quaternary ammonium hydroxide.

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