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Eliminating Solvents in Resist Removal Processes Using Low-Cost Detergents

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Abstract - **Cleaning processes may account for up to 25% of all steps in the manufacture of a microelectronic device [1]. According to the 2009 ITRS, ESH strategies include the reduction of chemical exposure, usage, and waste [2], and soon may consider building certification [3]. One simple way to move towards these objectives and save over 50% in costs is by replacing organic solvents with aqueous detergents to strip photoresist (PR). Positive-tone and negative-tone acrylic resins may be removed in seconds or minutes with aqueous detergents meeting performance and selectivity needs of the process. Aggressive systems of high alkaline strength (i.e. pH=14) can be built to perform as needed while metals and substrates are protected [4-6]. Successful aqueous chemistries provide good penetration, particle removal, and sheet rinsing while foaming is held in check. Detergents used at 3-10% by weight in water can offer superior performance, eliminate solvents, lower costs, and reduce waste.**

I. INTRODUCTION

Photoresist (PR) removal processes used in microelectronic manufacturing will typically finish with a water rinse. For this reason, it is practical to explore PR removal by aqueous means. Replacing organic solvents with aqueous concentrated detergents minimizes worker exposure, reduces waste, and can reduce raw material costs by over 50%.

PR removers are classified as a lithography ancillary. The market size of removers is dependent on PR usage. Global semiconductor PR usage accounts for ~$1bn USD revenue, which the majority represents positive tone [7]. Thin film transistor – liquid crystal display (TFT-LCD) panel manufacturing, where overall material consumption is 70% that of semiconductors, also uses positive PR. Although TFT-LCD usage volume may be high, a cost pressure and commoditization of this PR reduces the respective revenue to ~$250m USD. PR remover revenue is estimated to be ~35% of PR usage [8]. Calculating a global resist market at $1.25bn USD, the PR remover market is ~$450m USD. This value is considered a significant target to reduce costs by using aqueous detergents to remove PR.

A. Photoresist

Resists may be classified using a wide range of properties. Positive tone resists comprise hydrophobic/philic photoreactive systems based upon diazonaphthaquinone (DNQ) [9] and chemical amplifying (CA) [10]. Resin components of these systems include phenol-formaldehyde (novolac) and polyhydroxystyrene (PHOST), for the DNQ and CA system, respectively. The resins are hydrophilic (polar), allowing easy development following exposure. Other polar resist chemistries include negative tone acrylics (Table 1).

TABLE 1
Properties of polar chemistry PR resins.

Tone	Sensitizer & Resin	Resin Chemistry	Developer
Positive	DNQ Novolac	Thermoplastic	Aqueous (NaOH, KOH, TMAH)
Positive	CA PHOST	Thermoplastic	Aqueous (NaOH, KOH, TMAH)
Negative	Benzoin Acrylic	Thermoset	Aqueous (Na_2CO_3, K_2CO_3)

The resins in Table 1 are soluble in aqueous alkali suggesting their cured form should also be removed similarly. This would apply if no thermal or chemical excursions occur to cause polymer cross-linking. DNQ/novolac PR is primarily used for TFT-LCD operations. Novolac resin is polar and aqueous alkali soluble due to its hydroxyl functionality. DNQ controls the aqueous solubility of the system by its ability to convert from a non-polar form to a polar acid (Figs. 1-2).

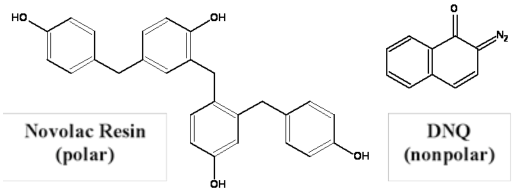


Figure 1. Novolac and DNQ polarity difference as the basis for PR function.

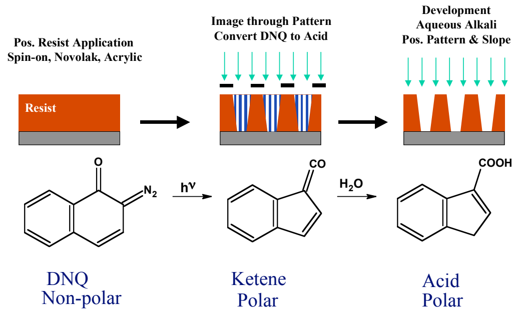


Figure 2. DNQ polarity conversion during PR processing.

TFT-LCD panels are processed on conveyor-type tools utilizing slit delivery of PR and spraying of chemicals. PR stripping occurs in seconds using a heated chemistry, typically 40-70˚C for 30-60 sec. A typical process flow is shown to include all steps from substrate cleans to PR stripping (Fig. 3).

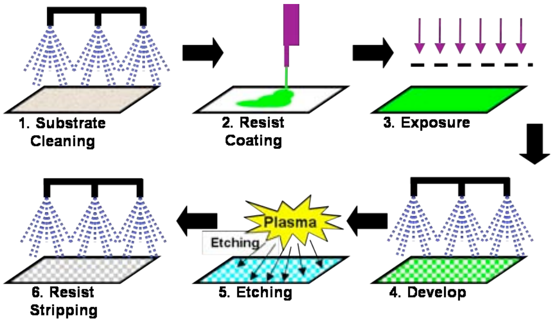


Figure 3. Typical flow for FPD lithographic processing.

In contrast to positive resists, negative-tone acrylics are cross-linked to form an impervious mask, a desirable condition for processes requiring high resistance. These chemistries involve methacrylate or styrenic resins with benzoin-based free-radical photoinitiators. PR formulations containing multiple monomer types will disproportionate, cross-link between chains, and increase density and hardness (Fig. 4).

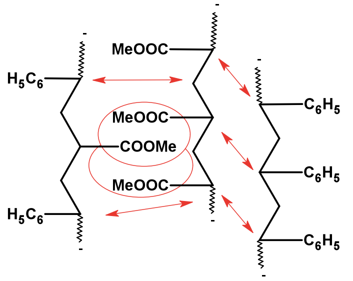


Figure 4. Free radical polymerization of methacrylate and styrene monomers to produce many combinations.

Another important quality of negative acrylics is their ability to generate thick patterns, a valuable property used in plating and forming solder bumps in back-end semiconductor packaging (Fig. 5).

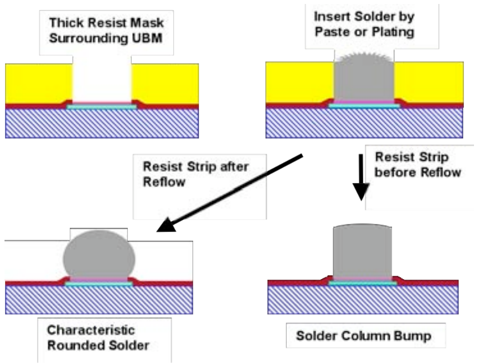


Figure 5. Solder bump process using liquid and dry-film PR.

The cured PR must withstand acid plating baths and solder paste that is reflowed at >200˚C. Removing negative PR produces serious challenges. Commercial strippers are commonly based upon organic solvents and aggressive alkalis. Processing temperatures are held at 100˚C for periods exceeding an hour, causing corrosion and other irregularities. The act of removing negative PR continues to burden throughput, yield, and cost in semiconductor manufacturing.

B. *Dissolution & Removal*

PR stripping processes use organic solvents to dissolve simple polymers (i.e. thermoplastics). Interaction starts with a polarity-driven "likes dissolve likes" approach, the character of solute and solvent are matched. Dissolution proceeds by the *infiltration* model, where solvent diffuses, infiltrates, forms gels, breaks-up the polymer and transports to the bulk media, and repeats until dissolution is complete [11].

When the solute is cross-linked, reactive chemistries must break bonds and release the solute to the bulk medium. Reactive materials include acid/base, complexing, and redox (reduction-oxidation) agents. For example, an acrylic resist is broken down by neutralizing residual acid character of the resin using tetramethylammonium hydroxide (TMAH, Fig. 6).

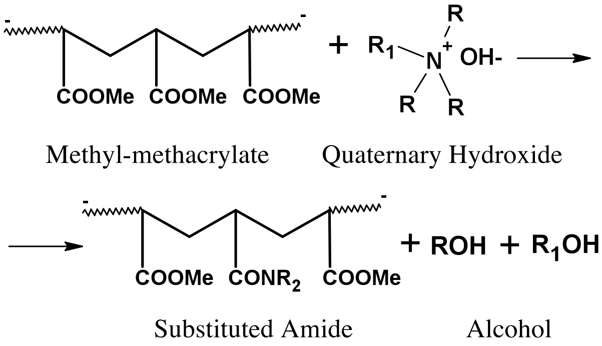


Figure 6. Breakdown of cross-linked acrylic polymer by TMAH.

TMAH hydrolyzes bonds between methacrylate resins while the solvent assists in penetrating the overall system. These pathways work together to swell the system, increase surface area for alkali action, hydrolysis, and form soluble amides and other simple molecules rinsed by the solvent.

Next to chemistry, temperature is the quickest way to improve dissolution. Heat is expected to accelerate dissolution by a factor of 2 for every 10 ºC rise in temperature as explained by the Arrhenius equation. Agitation is the next option to improve dissolution by increasing motion of the solvent molecules and reduce the boundary layer between solute and solvent. Available agitation technologies include simple mixing, spraying, and ultrasonic cavitation.

C. *Corrosion Inhibition*

Inhibitors are required in aqueous formulas where sensitive metals and substrates must be protected. For example, benzotriazole (BTA) and tolyltriazole (TTA) are well known adsorptive copper inhibitors [12]. These are commonly incorporated into formulations where resists must be removed from Cu containing substrates. Mixtures of BTA and TTA can be made synergistically to maximize surface passivation while minimizing thickness to <10Å [13]. The mechanism for BTA's unique film forming effect on copper is suggested to be a planar structure of stoichiometry 1:1 Cu:BTA based upon work with cupric and cuprous-BTA complexes [14] (Fig. 7).

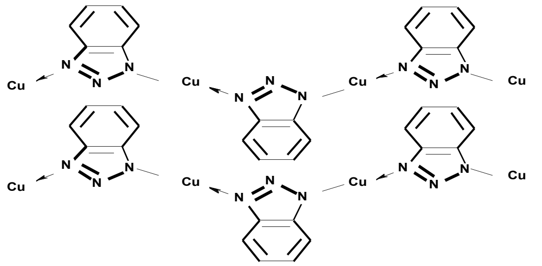


Figure 7. Planar structure of Cu:BTA, passivation for Cu.

Many inhibitors are specific to the metal, operating as a "lock-and-key." One example is in the formation of aluminosilicates. Silicates are chemisorbed onto aluminum to produce an inert coating, resistant to alkaline conditions [15]. Other inorganic inhibitors include phosphates. Organic groups with carbonyl character are known to provide metal chelating and protection, as found in citrates and pyrolles (Fig. 8)

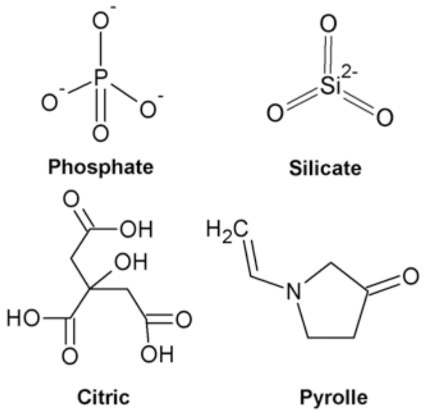


Figure 8. Example inhibitors for transition metals.

Corrosion is controlled by chemistry, temperature, and conductivity. Solutions of high water content with ionic substances are inherently more likely to cause corrosion. Investigation of stripping solutions used to remove PR from aluminum devices on TFT-LCD panels indicates both corrosion and conductivity increase with water content [16]. When rinsing a simple organic-amine stripper, aluminum corrosion increases from ~100 Å/min to >800 Å/min as water increases from 50% to 90% (Fig. 9).

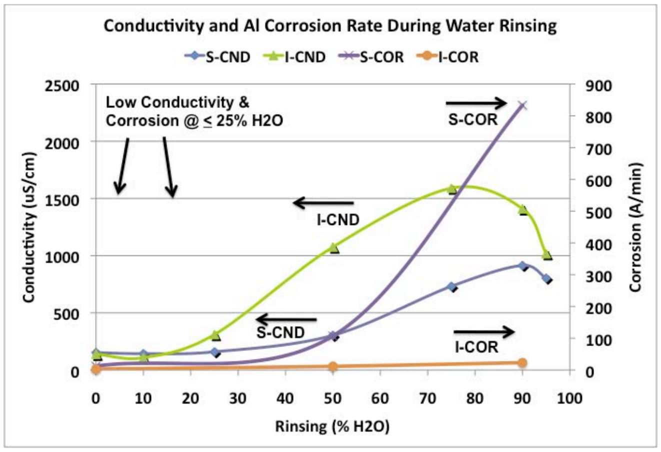


Figure 9. Conductivity and corrosion rate vs. water content during rinsing. S-CND I-CND = conductivity for stripper & inhibited stripper, respectively; S-COR, I-COR = corrosion for stripper & inhibited stripper, respectively.

Inhibited systems may show a rise in conductivity with water content, however, corrosion remains unchanged. In Figure 9, the inhibited stripper (I-CND & I-COR) exhibits a higher conductivity with water content, but corrosion is low, near baseline. This is explained by inhibited systems to contain ionic chemistries described in Fig. 8, which increase conductivity while passivating metals.

D. PR Strippers

Specialty chemical formulations are designed to enhance dissolution characteristics and offer selectivity when sensitive areas exist on the substrate or preferential removal of one polymer over another is necessary. Formulations may also contain reactive species when bonds must be broken or substituents on the polymer molecule must be converted to other forms to enable the overall system to become more soluble.

Most formulations involve a solvent, co-solvent, and surfactant package composed of materials having different hydrophobic/philic and organic solvency properties. These materials perform synergistically together enabling superior properties beyond that exhibited individually. Low viscosity and surface tension allows penetration and wetting of surfaces by contact angle reduction. By combining these characteristics, condensed polymers may be swelled, emulsified, suspended, and surrounded by stripper ingredients to enable easy rinsing and prevent redeposition. Additionally, their low foaming character offers greater efficiency for capillary action to small dimensions during a variety of agitation conditions practiced by tools used in a Fab.

E. Aqueous Systems

The primary reasons in using aqueous cleaning practices include environmental safety and cost reduction. Aqueous detergents are non-flammable, non-toxic, and do not generate evaporative material to trigger air permit requirements. Aqueous cleaners are available in concentrated forms as liquids and solid powders. The concentrate is diluted into water, typically 3-10%. Once the product is mixed and filtered, it is ready for use, unless heating is necessary. Using detergents for PR stripping is the fastest way to reduce costs of raw materials by as much as 50%, and further, to reduce or eliminate the need for waste management.

Many subtleties exist in aqueous cleans, and many believe it to be more challenging to control than organic solvents. Effective aqueous systems are built with additives that prevent irregularities during processing. Certain detergents may be mixed with tap water while rinsing with purified water. Ingredients in the detergent mix with contaminants in tap water to prevent metal precipitation, inhibit corrosion, and stop scale build-up. Because aqueous strippers become dirty during use, it makes sense to reduce water use and lower operating costs by reserving purified water for rinsing.

Detergents are being accepted for high performance PR stripping and selectivity, especially where large substrates are being processed. Introducing aqueous detergents in such cases can be successful, provided that a close match is met between chemistry and the process.

II. EXPERIMENTAL

A. Materials and Equipment

Photoresist and patterned substrates are supplied or arranged internally. Semiconductor wafers (200mm) were coated with between 80-120um of negative acting resist (acrylic). Liquid PR is based upon JSR THB-151N [17] while dry-film is based upon DuPont WB-100 series [18]. Patterned wafers were processed to contain in-via solder studs on a sputtered seed metal Cr/Cu (50/150 nm) film. PR was applied by spin or print coating, respectively for liquid and dry-film, PAB, and exposed to 1000-1100 mJ/cm^2 of radiation @ 420 nm, developed in preferred alkaline chemistry to produce >140 µm diameter hole size patterns, and PEB at temperatures >150 °C. The plated bumps are Pb/Sn (95/5) and of a height >50 µm.

LCD substrates used low sodium glass with sputtered Al alloy at <10,000 Å = 1um. The Al sputtered glass was slit-coated with AZ-P4620 PR [19] achieving a thickness of <3 um, PAB, exposed, developed, and PEB in preparation for aluminum etch using a mild RIE process. The patterned substrates are used for PR removal demonstration. Coupons used for metal safety tests included 200mm silicon wafers deposited with copper or aluminum sputter plating (10,000 Å) on a tantalum seed (250 Å).

Metrology support was conducted with an Ambios XP-1 manual profilometer, using a 5 nm carbon tip stylus. Specimens scheduled for SEM analysis were Pt coated and analyzed by a Hitachi 4700 SEM. Surface tension was measured with a Fisher DuNuoy Pt ring instrument.

III. RESULTS

General target performance of aqueous PR stripping solutions is measured as the ability for the chemistry to dissolve and remove a novolac coating within 15 and 30 seconds at room temperature. A series of aqueous chemistries were prepared containing alkalis of varying concentration and strength, with a solvent used as a reference condition. Concentration is measured as normality (e.g. 1 normal = 1 equivalent/liter concentration), while strength is measured as pH. Results are given in Table 2.

TABLE 2
Stripping results of AZ P4620 DNQ novolac PR on FPD glass, 15 & 30 sec, room temperature (~20 °C).

Chemistry	**Normality**	**pH**	**15 sec**	**30 sec**
Alkanolamine, solvent	0.5	10-11*	Clean	Clean
Alkanolamine, aqueous	0.5	10-11	No clean	No clean
TMAH, aqueous	0.26	14	No clean	No clean
KOH, aqueous	0.1	14	Clean	Clean

* Measured as 1:1 solution in water

A blanket coated and cured PR film similar to that expected for TFT-LCD applications is dissolved and removed within 15 seconds using simple solvent mixtures. The same alkali at the same concentration of 0.5N and dissolved in water does not clean within 30 seconds. Using aqueous chemistries of increased strength (pH=14) produces mixed results. An organic hydroxide, TMAH 0.26N, produces no clean, whereas KOH, an inorganic hydroxide present at <50% (i.e. 0.1N), is clean. DNQ/novolac PR exhibits both organic character and the ability to dissolve in aqueous alkalis. Although different species may exhibit similar ionic strength (i.e. pH=14), their reactivity is dependent upon diffusion-limited phenomena such as solution mobility. The relative ionic size of TMAH to KOH is more than 2X, which helps explain the slow stripping reaction of TMAH.

Stripping PR is a stepwise process, which merges removal with rinsing. Water rinsing is always preferred, however, the surface tension of water is high, making it difficult to ensure small spot geometries to be clean. Low surface tension rinsing ensures good penetration, mixing, dispersion, and reducing residues. The data in Fig. 10 indicates that a formulated detergent can maintain lower surface tension during rinsing as compared to solvent-based strippers.

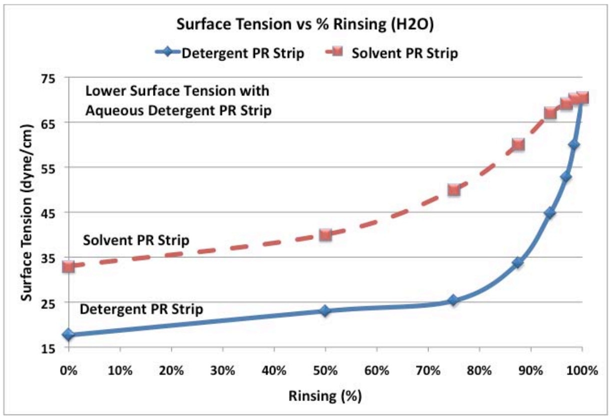


Figure 10. Surface tension of detergent vs. organic solvent during rinsing.

One of the most important properties of formulated systems is their selectivity, or protection of sensitive metals during performance. Figure 11 presents an organic solvent stripper, of moderate alkalinity, similar to that identified in Table 2. At this alkalinity (pH=10-12), the organic stripper exhibits accelerated corrosion during water rinsing at mixing levels of 80-95%. The formulated detergent exhibits higher alkaline strength, yet provides near non-detectable corrosion throughout rinsing.

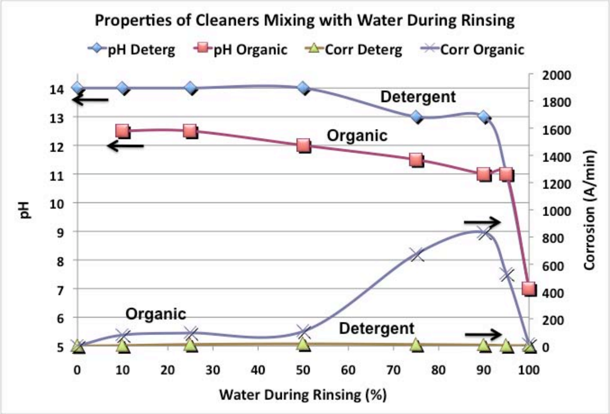


Figure 11. Al corrosion and pH of detergent and organic during rinsing.

Chemical additives preferred for detergent formulas will reduce surface tension while maintaining low foam during aggressive agitation or spray conditions. Whenever possible, the use of defoaming agents should be discouraged, as these systems are designed to disrupt the fluid boundary through insolubility. Insoluble species such as silicones, heavy hydrocarbons, and nano-particles, albeit are ideal for industrial applications, are difficult or impossible to control for critical clean substrates. Preferred choices include the use of surfactant cloud point matching to a process, low-foaming fluorocarbons, and mixtures thereof with phosphate esters.

Figure 12 describes the use of a variety of surfactants added to detergent matrix in water, including hydrocarbon (nonionic), fluorocarbon (nonionic), phosphate ester (anionic), or mixtures. Surface tension reduction (bars, left axis) suggest all of those tested work well except phosphate esters. The same products tested for foam production (lines, right axis) indicates that phosphate esters or mixtures are best.

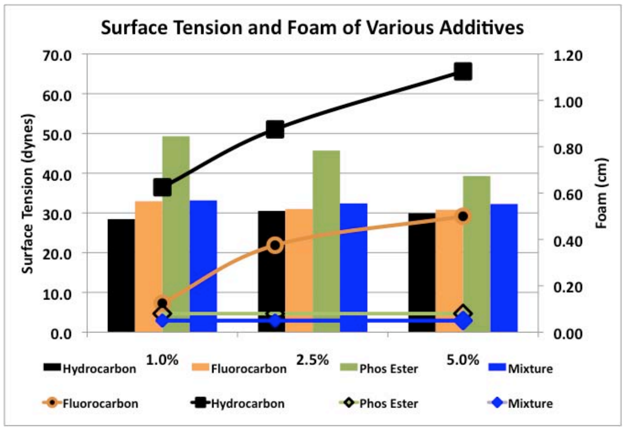
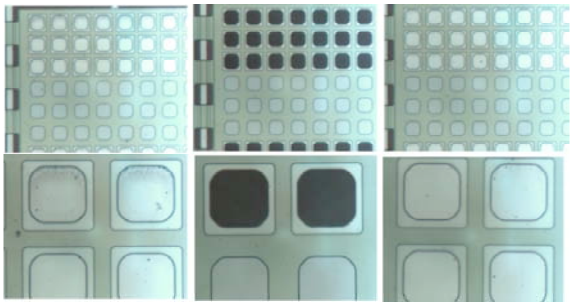


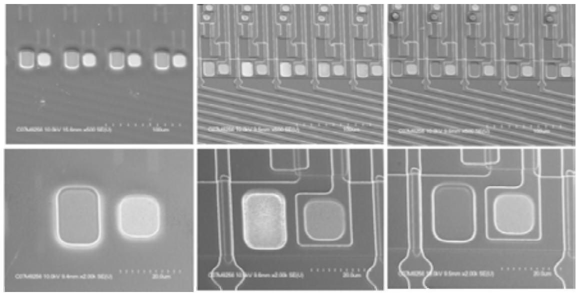
Figure 12. Surface tension and foam observations of detergent additives.

TFT-LCD patterned glass parts were tested using a non-inhibited detergent and the same built with an inhibitor. Both cases practice a 5% dilution by weight in water, 30sec @ 50-60 ˚C, rinse in DI water and dry. Optical and SEM results show Al corrosion for non-inhibited and protection for the inhibited system (Figs. 13-14).



PR (before) Strip (non-inhibited) Strip (inhibited)

Figure 13. Optical photos of TFT-LCD Al devices, before strip (left), non-inhibited detergent (middle), inhibited detergent (right).



PR (before) Strip (non-inhibited) Strip (inhibited)

Figure 14. SEM photos of TFT-LCD Al devices, before strip (left), non-inhibited detergent (middle), inhibited detergent (right).

SEM photos are shown in Figure 15 of negative-tone acrylic PR of the form: liquid (top) and dry film (bottom). Both series represent an electroplated solder bump. PR stripping is conducted using an inhibited detergent, 5% by weight in water, <5min @ 90 ˚C, water rinse, and dry. Using detergents to remove PR does not result in dissolution, rather, the PR lifts off from the substrate in pieces and disperses in the solution where it is filtered away. When the process is optimized, no measurable residue is apparent. Typical solvent strippers require >30min, and many times >1hr, at similar temperatures.

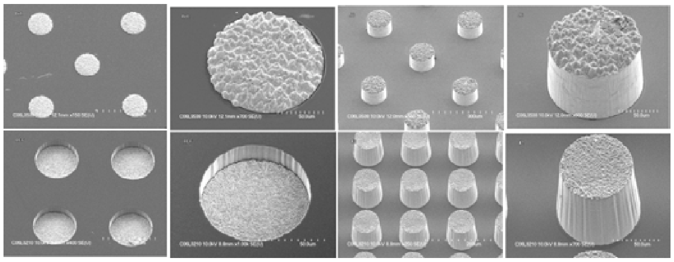

PR – low mag PR – high mag Strip – low mag Strip – high mag

Figure 15. SEM photos before and after stripping of 95-5 solder plating in JSR liquid PR (top photos) and DuPont Riston dry-film PR (bottom photos).

IV. DISCUSSION

Detergents used to strip PR must incorporate aggressive ingredients such as KOH to effectively remove the mask within seconds or minutes, inhibitors and surfactants as fluorocarbons or mixtures thereof. These materials must work together as a system to successfully model and improve the efficiency of solvent stripping. Positive DNQ/novolac PR is removed within seconds as demonstrated on processed TFT-LCD panels. Cured negative acrylic PR for solder processes is effectively removed in a fraction of the time as seen by solvent strippers.

Introducing detergents for PR stripping require an attractive cost package. Minimum requirements in the TFT-LCD market suggest a material cost reduction of 50%. Additional cost incentives to this savings include process safety and eliminating offsite waste treatment. These benefits and options for variable mixing and replenishment offers flexibility during process integration.

V. CONCLUSIONS

This paper presents data on formulating and process demonstration for successful integration of aqueous detergents for PR stripping. Using a solvent chemistry as a benchmark for replacement is key for performance and cost comparisons. With proper chemistry and process matching, detergents can be used to remove PR while protecting the substrate during rinsing. A minimum cost reduction of 50% is a valid target for materials savings while many other benefits begin to weigh-in after integration, including safety, waste minimization, and achieving green factory certifications.

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