

High loading capacity solvent blend for a safe and efficient alternative to NMP and amine-based strippers

Diane Bijou^{1, a}, Robin Douville¹, Anaïs Passelande¹, Marine Audouin¹, Lorian Céleste¹, Harold Le Tulzo¹, Jérôme Daviot²

¹ Technic France, 15 rue de la Montjoie, F-93212, Saint-Denis, FRANCE

^a diane.bijou@technic.fr

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Introduction

For photolithography processes, a wide variety of photoresists (PR) are employed, and large volumes of chemicals are thus required for their removal. Due to their poor reticulation, positive PRs are usually dissolved using solvents or solvent blends which include solvents like N-methylpyrrolidone (NMP) and dimethyl sulfoxide (DMSO). However, these solvents present several drawbacks, such as limited loading capacity, in addition to NMP reprotoxicity, and high melting point of DMSO. Moreover, in advanced packaging applications, thick photoresists (> 10 µm) are increasingly demanded to achieve structures such as copper (Cu) pillars and through-silicon-via (TSV) microbumps [1]. While negative tone PRs are generally preferred [2], new high-performance positive photoresists are more and more used to facilitate stripping compared to negative resists [3]. Yet, their large thickness leads to low loading capacity when using conventional solvents or solvent blends. To mitigate rapid bath saturation, particle formation, and incomplete stripping, more advanced strippers, such as amine-based or tetramethylammonium hydroxide (TMAH)-based formulations, are often employed. However, these last are less selective towards aluminum and/or copper and in case of TMAH-based stripper, less effective regarding very thick positive PR. In addition, the use of TMAH is increasingly restricted due to its high toxicity. To address industry's demand for high-performance and safe stripper, a new solvent blend has been developed. Its performance was extensively evaluated and benchmarked against industry-standard products in terms of stripping rate, metal selectivity, and loading capacity.

Results

Following NMP potential ban in EU, semiconductor industry focused on finding an affordable and performant solvent replacement. To identify a molecule as efficient and versatile as NMP, chemical producers based their research on solvent parameters such as Hildebrand or Hansen Solubility Parameters (HSP) [4]. This led to emergence of several new solvents such as dihydrolevoglucosenone (CyreneTM), N-butylpyrrolidone (NBP) or N-formylmorpholine (NFM). These candidates were included in a comprehensive study, screening over 70 solvents where stripping performances were evaluated on three challenging PRs. However, none of these promising solvents matched the efficiency of NMP, indicating a limited correlation between HSP and stripping performances. Overall, no alternative was found but several solvents mixed with DMSO succeeded to be as efficient as NMP. Among these, one particularly promising solvent was selected to be mixed with DMSO and other components to meet specifications. Then, their concentrations were fine-tuned to optimize properties which led to the creation of a new solvent blend with no hazards statement: TechniStrip[®] 680. The performances of this new stripper were then evaluated using a thick positive photoresist and benchmarked against pure solvents and industry-standard products, such as a DMSO/Gamma-butyrolactone (GBL) mixture and "reference" being a DMSO/amine-based stripper. For each stripper, the time to clear the resist and the loading capacity were determined at 65 °C, and reported in Figure 1.

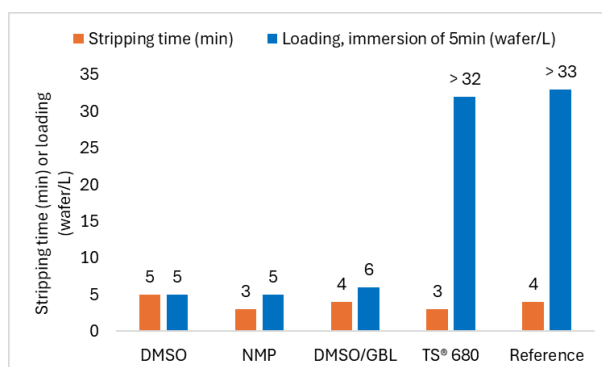


Figure 1: Stripping and loading performances of various strippers using the photoresist TOK PMER 4000, 37 μm -thick, deposited on 200 mm silicon wafers. Experiments performed at 65 $^{\circ}\text{C}$, with a gentle stirring (250 rpm), and direct deionized water rinsing. “TS[®] 680” stands for TechniStrip[®] 680.

With a stripping time of 3 minutes, TechniStrip[®] 680 exhibits a significantly faster stripping rate than DMSO and DMSO/GBL mixture, while ensuring a better surface cleanliness. Its stripping performances are more comparable to NMP, confirming initial results, but TechniStrip[®] 680 offers an enhanced loading capacity, similar to DMSO/amine-based strippers. Its superior capacity to dissolve and disperse photoresists was confirmed using turbidity measurements and a loading capacity over 50 wafers/L was found for another thick positive photoresist. Although each component of TechniStrip[®] 680 is a less efficient stripper on its own than the blend, the combination achieves remarkable efficiency. In addition, neither calculated HSP of the solution nor its components HSP align with NMPs' values. Moreover, as mentioned previously, solvents with HSP close to NMPs' HSP are not necessarily efficient strippers. These results demonstrate that matching NMPs' HSP is not an effective method to find a high-performance stripper.

TechniStrip[®] 680 also proved to be highly efficient to strip thin positive photoresists as well as lift-off negative PR, and few examples are presented on Figure 2. Additionally, another study focused on effect of additional water (up to 5wt.%) on strippers' performances using three different positive PR. Regardless of adsorbed water concentration, TechniStrip[®] 680 succeeded to maintain a low contact angle after stripping, and unlike TMAH/amine-based strippers, the solution stayed highly compatible with most metals and dielectrics, including copper and aluminum.

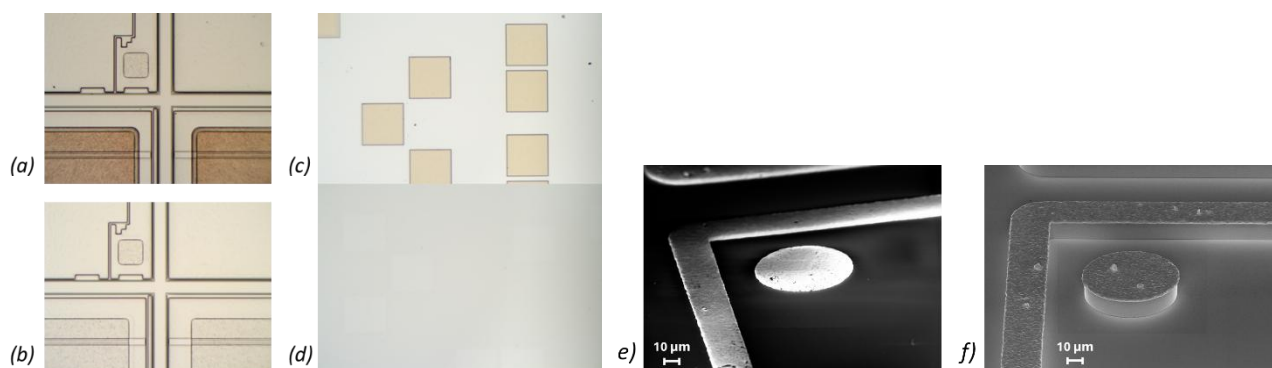


Figure 2: Optical microscope pictures of two stacks (magnifications X20 and X10): (a) with 6.5 μm -thick TOK positive resist and (b) after TechniStrip[®] 680 stripping (5 min at 65 $^{\circ}\text{C}$), (c) with 7 μm -thick P-tone resist and (d) after TechniStrip[®] 680 stripping (1 min at 30 $^{\circ}\text{C}$). SEM images of a structure made of a 15 μm -thick TOK PMER P-CE5000 photoresist with Cu/Ti/Sn bumps (e) before and (f) after immersion in TechniStrip[®] 680 during 5 min at 20 $^{\circ}\text{C}$.

Conclusion

To conclude, a new solvent blend, named TechniStrip[®] 680, was developed to target a large variety of photoresists from thin positive to negative lift-off, including uncured polyimide. It offers stripping performances of amine/TMAH-based strippers while being compatible with sensitive metals like AlCu and Cu. Easy to handle with a low freezing point, TechniStrip[®] 680 is also not classified dangerous and is label-free, ensuring better workplace safety and environmental compliance. Its outstanding loading capacity makes it particularly suitable to strip thick positive photoresists. With longer bath life, chemical consumption and waste can be greatly reduced and thus cut costs in case of high-volume manufacturing. Altogether, TechniStrip[®] 680 features make it compatible with various processes and thus a perfect candidate to replace hazardous strippers.

- [1] J. H. Lau, IEEE Trans. Compon., Packag. Manufact. Technol., vol. 12, no. 2, p. 228-252 (2022).
- [2] H. Sakakibara et al., 16th International Conference on Electronic Packaging Technology, p. 1348-1351 (2015).
- [3] H. Sohn et al., Solid State Phenomena, vol. 219, p. 225-229 (2015).
- [4] M. C. Bryan et al., Green Chem., vol. 20, no. 22, p. 5082-5103 (2018).