Naphta-free organic acidic-based stripper for highly hydrophobic polymers removal

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Polyisoprene-based photoresists emerged in the 1950s as a system of choice to perform photolithography processes [1]. These materials are formulated by mixing photoactive bis-arylazides with low molecular weight synthetic rubbers [2]. As a negative tone photoresist, it becomes insoluble in developer when exposed to light, due to the cross-linking of bis-arylazides with cyclized poly(cis-isoprene) (Figure 1). Although its low resolution (2 µm) led to its gradual replacement by newer materials, such as positive tone Novolak-diazonaphthoquinone-based photoresists, polyisoprene-based photoresists remain in use. The industry values them for their reliability, cost-effectiveness, excellent adhesion, and high chemical resistance, which are crucial for plating and wet etching processes. Notable examples include SC and HNR resists supplied by Fujifilm, and the OMR series supplied by Tokyo Ohka Kogyo [3,4].

Strippers of polyisoprene-based photoresists typically consist of a mixture of an aromatic naphta distillate and an alkylaryl sulfonic acid molecule, referred to as "industry-standard". Additives, such as polyhydroxyphenols like catechol [5] and resorcinol [6], may be included to enhance metal compatibility. These mixtures offer efficient resist removal and demonstrate a fairly good compatibility with a broad range of materials, including III/V semiconductors and most metals. Nevertheless, they have significant drawbacks. Indeed, these industry-standard products are often considered harmful due to residual naphthalene content from the naphta distillate, and the use of polyhydroxyphenol-based inhibitors. Catechol has been proven to be carcinogenic and is also suspected to be mutagenic, while resorcinol can damage organs, particularly the nervous and respiratory systems. Additionally, the strong smell of these petroleum-based mixtures can be unpleasant, and their high viscosity can make them difficult to rinse.

To the best of our knowledge, historical solvent alternatives are limited to acetone and anisole, which are highly volatile organic chemicals, chlorinated hydrocarbon solvents, formerly used but carcinogenic and toxic for the environment [3,5].

To address these issues, a screening of solvents and corrosion inhibitors has been conducted, evaluating their stripping efficiency and metal compatibility based on the chemical functions of the tested molecules. The study of the solvents' chemical structures revealed that shorter alkyl chain lengths correlated with higher stripping efficiency, as less process time was needed to thoroughly clean the samples (Figure 2). Furthermore, the presence of an alcohol functional group significantly enhanced stripping efficiency (Me-R versus Me-R-OH). After selecting the optimal molecules, their concentrations were fine-tuned to optimize properties such as reducing the etch rates of sputtered nickel by adding the appropriate concentration of a corrosion inhibitor (Figure 3).

This process led to the development of TechniStrip® D-Micro NGA883, an innovative organic surfactant-based stripper specifically designed for stripping polyisoprene-based photoresists. Optical microscope images and contact angle measurements demonstrated that TechniStrip® D-Micro NGA883 performs on par with, or even exceeds, industry standard solutions at 75 °C (Table 1). The process window of the formulation ranges from 75 to 100 °C for optimal performances. Additionally, it exhibits complementary capabilities, including the dissolution of benzocyclobutene (BCB) polymer, and the removal of polyimide. The solvents and additives in TechniStrip® D-Micro NGA883 are plant metabolites, providing an alternative to petroleum solvent-based industry-standard products. Being free from naphthalene and catechol, the TechniStrip® D-Micro NGA883 provides high removal capabilities while improving environmental, health, and safety (EHS) aspects, offering a pleasant plant fragrance, and enhancing loading capacity (Figure 4(a)). Furthermore, it is compatible with most metals and dielectrics (Figure 4(b)).

Figures & Table

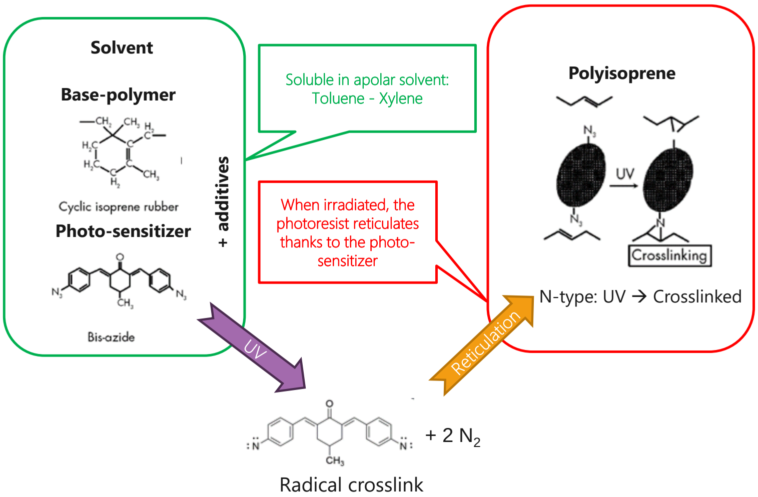


Figure 1 – Polyisoprene-based photoresist composition and cross-linking reaction.

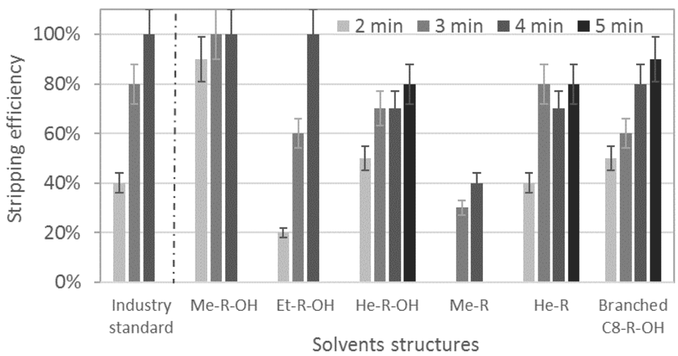


Figure 2 – Stripping efficiency of SC resists with various mixtures consisting of a solvent and an alkylaryl sulfonic acid molecule, performed at 90 °C for different immersion times with gentle stirring. The solvent alkyl chain length was varied, as well as the presence or not of an alcohol functional group, while keeping the same R structure. "Me" stands for methyl, "Et" stands for ethyl, "He" stands for hexyl.

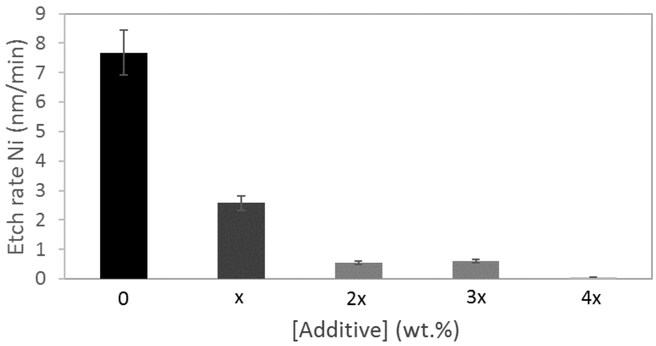
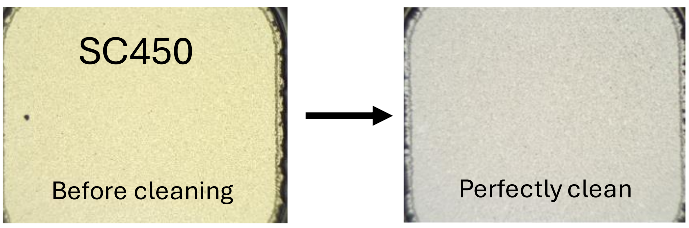
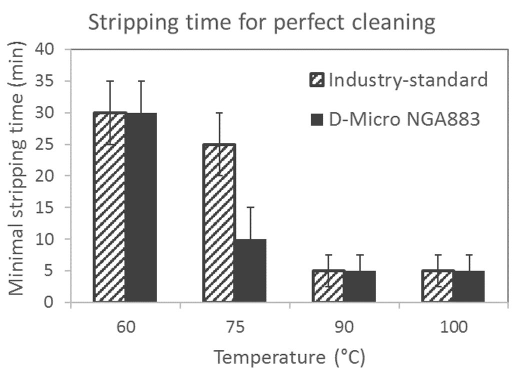


Figure 3 – Etch rate values for a sputtered nickel, obtained with a four-point probe, as a function of the additive concentration in a solvent-alkylaryl sulfonic acid mixture, at 90 °C with gentle stirring for a 10 min-long process immersion time.

Table 1 – Composition, hazard statements and process window differences between an industry standard solution and TechniStrip® D-Micro NGA883.

<table>
<tr><th></th><th>Industry standard</th><th>TechniStrip® D-Micro NGA883</th></tr>
<tr><td>Solvent</td><td>Hydrocarbon, naphthalene residues</td><td>Plant metabolite, used in fragrance and cosmetics. Naphtalene-free.</td></tr>
<tr><td>Additive 1</td><td>Polyhydroxyphenol</td><td>Plant metabolite, used as a food additive</td></tr>
<tr><td>Difference of hazard statements</td><td>H304 - May be fatal if swallowed and enters airways

H350 - May cause cancer

H361 - May cause damage to organs
</td><td>H302 - Harmful if swallowed
</td></tr>
<tr><td>Photoresist stripping capability (optical microscope images)</td><td colspan="2">
</td></tr>
<tr><td>Process window for stripping of SC resists</td><td colspan="2">
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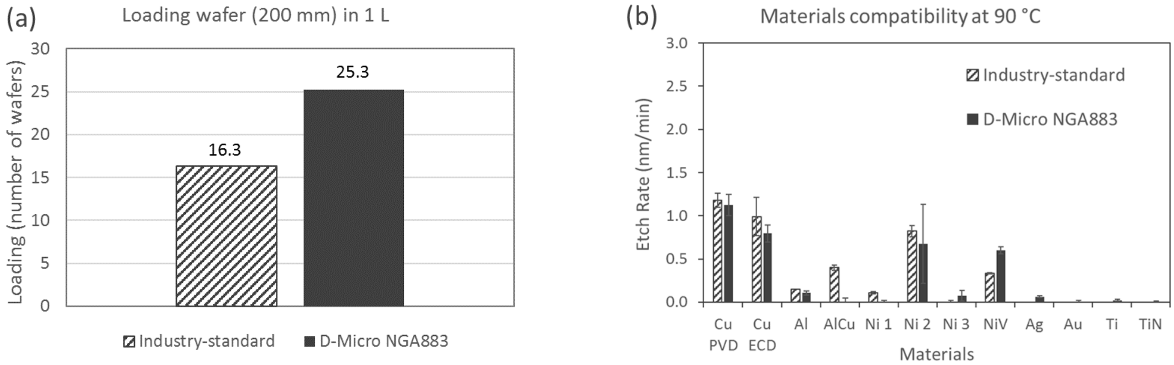

Figure 4 – (a) Loading capacity with SC series resists obtained at 90 °C, and compared to an industry-standard solution. (b) Etch rate values for metals and dielectrics obtained with a four-point probe after immersion in an industry-standard solution and TechniStrip® D-Micro NGA883 at 90 °C.

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