Process 2.4

# *Photoresist Stripping of Wafers*

## *1.0 Process Summary*

**1.1** Total removal of photoresist is often desired after a photoresist pattern has served its purpose in etch or deposition masking. Several byproducts of wafer processing can cause a photoresist to be difficult to strip, and many solutions that are capable of stripping such “toughened” resists also put delicate metals and other structures at risk of attack from the stripping solution.

## *2.0 Material Controls & Compatibility*

**2.1** There are several methods for photoresist stripping and appropriate consideration of the materials on your substrate must take place prior to using a photoresist strip process.

**2.2** Remember to check the etch rate of any exposed material before designing a process flow to include a strip bath. Plasma O2 stripping will attack several kinds of material, and photoresist stripping materials will often attack metals or other polymers on your substrate without proper consideration before processing.

## *3.0 Applicable Documents*

**3.1** List related documents and manuals.

## *4.0 Definitions & Process Terminology*

**4.1** Photoresist stripping: Total removal of photoresist by a given process

**4.2** O2 Ashing: Removal of photoresist via heat and activated downstream oxygen plasma.

**4.3** Strip Bath: A chemical bath designed for immersion of wafers during the strip process

**4.4** Plasma Byproduct: A Teflon-like byproduct of CF4, CHF3, CH3F, and C4F8 plasmas.

## *5.0 Safety*

**5.1** Follow general safety guidelines for the lab; the safety rules outlined in **Chapter 1.01 - Marvell NanoLab Chemical Hygiene Plan** and the following:

**5.1.1** Nearly all wet chemistries in photoresist stripping can be dangerous if exposed to skin.

**5.1.2** Always wear the following safety gear: Apron, face shield, chemical-resistant gloves. Never walk around the lab with chemical gloves on to prevent unintentional transferring of chemicals to surfaces and door handles throughout the lab.

**5.1.3** Pre-heated baths:

**5.1.3.1** Msink1 and 2 contain the 1165 Remover, and pre-metal clean solution SVC-14. All of these chemistries have flash points specified in the material data sheet. Do not adjust the heater controllers as they have been preset to produce proper temperatures for these chemical solutions currently at 80ºC.

**5.1.3.2** When using cassette processes, only use the white Teflon® 25-slot chemically resistant cassettes with locking handles provided for the sink you are using. These cassettes are dedicated to each sink and are not allowed to be used elsewhere in order to prevent cross-contamination. Failure to use these cassettes with locking handles can compromise the operator’s safety.

**5.1.3.3** The de-ionized (DI) water deck hose for the sinks is ALWAYS available for emergencies; it provides a good safety backup in the event of exposure to chemicals.

## ***6.0 <u>Process Data</u>***

**6.1** Comparison of NMP based photoresist stripping compounds after short soak (30 minutes) in strip bath:

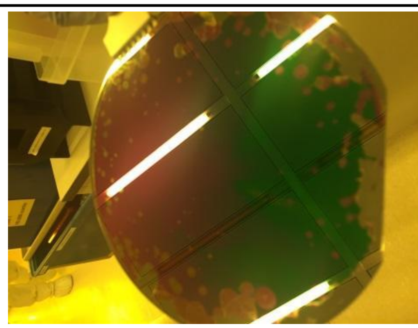
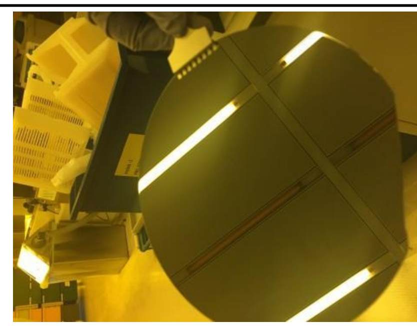
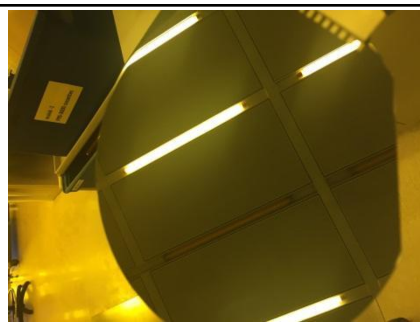
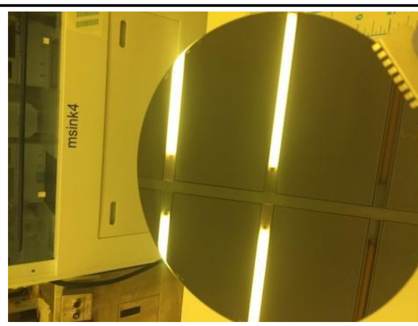
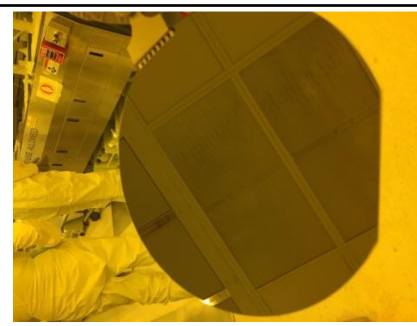
| Strip Solution | DUV w/ UV Bake | i-line 150C oven harden |
|---|---|---|
| 100% NMP, 80C |  |  |
| PRS-3000, 80C<br>(30-50% Thiophene<br>40-50% NMP<br>5-15% 2-propanol, 1-amino) |  |  |
| 1165 Remover, 80C<br>(94-95% NMP<br>5-6% Pyrrolidinone Compound) |  |  |

Table 1. Qualitative resist strip processing results of i-line and DUV210 resist in various solutions at 80C after 30 minutes of immersion into a tank.

## *7.0 Process Explanation*

**7.1** Wet Strip Processing: Most photoresist stripping strategies focus on a wet chemistry approach.

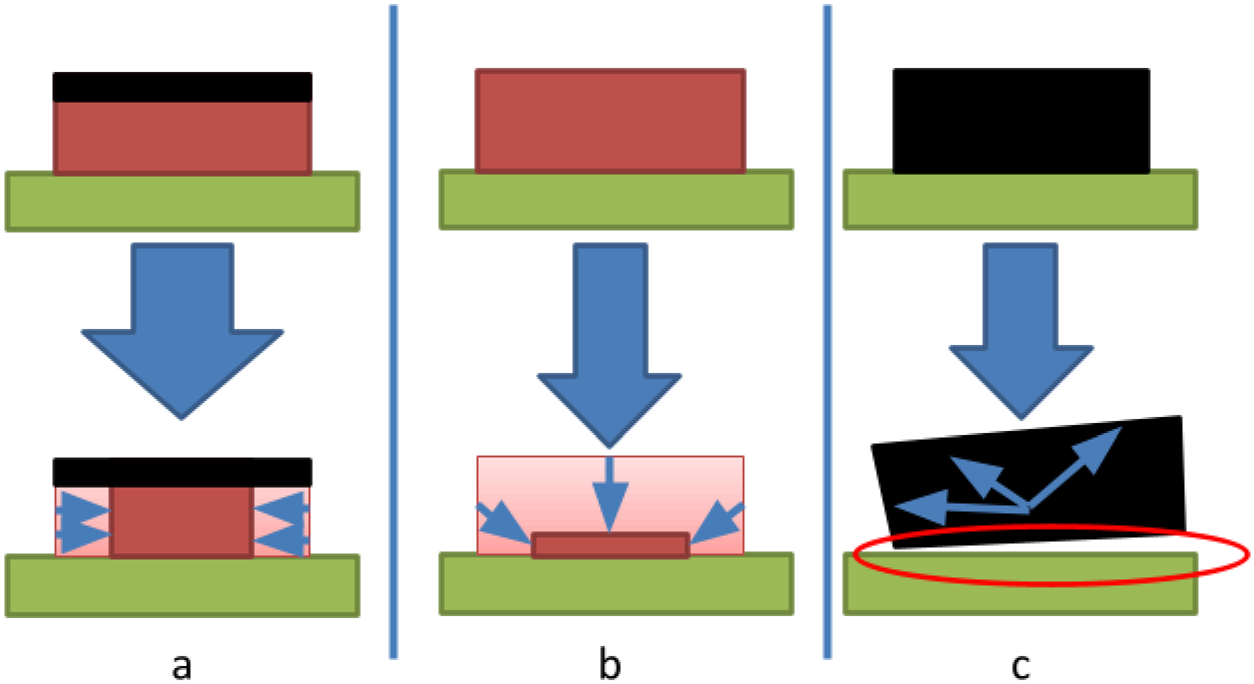



Figure 1. Methods of removal: a) undercut of hardened layers or etch byproduct. b) Dissolution of photoresist. c) swelling of photoresist and resulting fracture at interface of photoresist.

**7.1.1** Undercut

**7.1.1.1** Photoresist-wafer interface is attacked laterally from the nearest feature which penetrates through the resist layer. Lifts bulk photoresist off of the wafer

**7.1.1.2** Pros: Able to remove some films which are nearly impossible to strip (e.g. SU-8, etch byproduct)

**7.1.1.3** Cons: Debris often redeposits on wafer – treat as lift off, use fixturing to hold wafer upside down.

**7.1.1.4** **Note: Lift-off processing is not to be confused with photoresist stripping by undercut, regardless of similarity. Liftoff processing is described elsewhere in the Nanolab equipment manuals.**

**7.1.2** Dissolution

**7.1.2.1** Photoresist is removed by solvent penetration and dissolution into the solvent bath. Redeposition is unlikely, though some residues may remain at the photoresist/wafer interface.

**7.1.2.2** Pros: Useful for blanket photoresist that has not been hard baked. Fast and easily used as a batch process.

**7.1.2.3** Cons: Not all materials are easily dissolved, and processing steps taken on masks often removes this option as an effective stripping method.

**7.1.3** Swelling and fracture

**7.1.3.1** Some highly crosslinked photoresists such as SU-8 cannot be dissolved, and simply swell in the presence of photoresist stripping solvent. These photoresists are instead removed by dipping in a solvent that causes significant swelling, which removes the resist via internal stresses that result in fracture along the wafer/photoresist interface.

**7.1.3.2** Pros: Significantly effective at removing large thickness resists (negative resists > 200 um thick). Fast and easily used as a batch process.

**7.1.3.3** Cons: Often leaves debris along pattern edges from incomplete removal. Follow up with ashing or chemical removal.

**7.2** Dry Plasma Strip Processing: This approach uses heat and reactive neutrals to attack the layer without exposing the substrate to liquid contact.

**7.2.1** Ashing

**7.2.1.1** Remote oxygen plasma is generated and flows across the wafer. This process is a high temperature (typically 250C) process, which causes the carbon in the photoresist to react into $CO_2$, removing the photoresist.

**7.2.1.2** Pros: Wafer residue is rare. Attacks nearly all carbon based masking agents and etch byproducts

**7.2.1.3** Cons: Heat cycling of the wafer can be outside of thermal tolerances. Ashing is a single wafer process and takes about 3 minutes per wafer, so time quickly stacks up in large batches. May require multiple cycles of ashing on thick films.

**7.3** Post-strip Cleaning: Photoresist stripping processes can leave behind residues from their interfaces which are immune to the stripping chemistry.

**7.3.1** **Note: Cleaning is not a strip process – it is used AFTER strip processing to remove any residues. Using cleaning solutions as a stripping agent on fully coated wafers can result in vigorous reactions and dangerous conditions.**

**7.3.2** Chemical Removal

**7.3.2.1** Piranha and other active acids or bases can react with photoresist masks and other organic materials to form soluble or vaporous compounds.

**7.3.2.2** Pros: Cleanest wafer surface after processing. Easily batch processed.

**7.3.2.3** Cons: Highly corrosive chemistries are often incompatible with critical substrate layers. Very slow process, best used on thin layers.

**7.4** Post etch residue removal

**7.4.1** Removal of plasma etch by-products from sidewalls is an issue that may require additional chemical etches. Nanolab users have successfully used the following products for sidewall post etch residue removal. Please consult process staff if you would like to sample these chemicals for your process.

**7.4.1.1** Microstrip 5002 - from Fujifilm

**7.4.1.2** EKC 265 and EKC 270, hydroxylamine based cleaner from DuPont. Note: EKC waste <u>**can NOT be disposed of in the Lab Organic Waste bottle!**</u>

**7.5** Wet Chemistry options:

**7.5.1** NMP

**7.5.1.1** Ingredients: 100% N-methyl-2-pyrrolidinone

**7.5.1.2** Mechanism of Strip: Dissolution of photoresist polymer

**7.5.1.3** Significant Known Issues: UV baked DUV resist has outer crust that does not dissolve due to excessive cross-linking. Blocks further permeation of NMP into bulk through hardened layers – leads to very slow removal rates from edge of pattern.

**7.5.2** PRS-3000

**7.5.2.1** Ingredients: 40-60% NMP, 30-50% Thiophene, 5-15% 2-propanol, 1-amino

**7.5.2.2** Mechanism of strip: NMP dissolution of photoresist polymer by unraveling of secondary bonding structure. Thiophene used to agitate and deliver NMP through hardened layers of UV baked photoresist as well as Teflon-like etch byproduct.

**7.5.2.3** Significant known issues: Does not actually dissolve etch byproduct – simply undercuts it. Can redeposit on wafer. Slowly etches aluminum when aluminum is hydrated. Quickly etches Tungsten if it has not been resting for 1 day after pour.

**7.5.3** 1165 Remover

**7.5.3.1** Known Ingredients: >95% NMP, <5% pyrrolidinone compounds

**7.5.3.2** Mechanism of strip: NMP dissolution of photoresist polymer by unraveling of secondary bonding structure. Experimental results show significant improvement over 100% NMP when tested on UV cured resists. Unknown if <5% pyrrolidinone compound content somehow improves penetration through UV cured layer.

**7.5.3.3** Significant Known Issues: Intermittently leaves minor residues near tweezer contact points on wafer. Lab members report some materials can corrode when rinsed with water after 1165 exposure, notably silver – IPA rinse has been identified as a solution to these issues. The act of mixing 1165 and water appears to be the cause.

**7.5.3.4** Photoresist strings are left on wafers that have gone through a UV Bake step.

**7.5.4** ACT line of products by Versum

**7.5.4.1** Fluoride containing PR Strippers and post-etch residue removers

**7.5.4.2** The Fluoride containing strippers and post-etch residue removers have not been evaluated or characterized by Nanolab. Only included here for reference.

**7.5.4.3** Pros: skimming the SiO2 surface, low application temperature

**7.5.4.4** Cons: may corrode metals and etch dielectrics. However, different pH products are out there that promise varying degrees of selectivity.

**7.6** Dry Strip Chemistries:

**7.6.1** Matrix O2 plasma

**7.6.1.1** Ingredients: See matrix manual for standard recipe

**7.6.1.2** Mechanism of strip: Ashing – extremely good at removing most resists <5 um.

**7.6.1.3** Significant known issues: Heating of wafer and exposure to O2 plasma species. Significant oxide growth occurs in Matrix on metal surfaces, leading to harsher surface treatments to obtain good ohmic contact between layers

**7.6.2** A note about plasma etchers: While many of the plasma etchers are capable of etching photoresist, only the Matrix is designed to strip thick photoresist. Intentional removal of photoresist in any other plasma tool is not acceptable unless directly approved by staff.

**7.7** Cleaning Chemistries: These chemistries are **never** to be used on films of photoresist prior to stripping with other chemistries. Many are **highly reactive** and pose a hazard when mixed with a full wafer of photoresist. Always complete a photoresist strip step prior to cleaning your wafer which has been exposed to photoresist.

**7.7.1** Piranha Clean

**7.7.1.1** Ingredients: 99% Sulfuric Acid, recharged with $H_2O_2$ activation

**7.7.1.2** Mechanism of cleaning: Chemical removal via oxidation reaction

**7.7.1.3** Significant known issues: Actively attacks many metals and oxidizes silicon, leaves sulfur contamination on surface if not followed by HF dip, which attacks most oxides.

**7.7.2** SVC-14

**7.7.2.1** Ingredients: <60% DMSO, >40% cyclic ester

**7.7.2.2** Mechanism of Strip/Cleaning: Dissolution of photoresist. DMSO penetrates toughened layers quickly.

**7.7.2.3** Significant Known Issues: SVC-14 costs 2x as much as NMP based solutions, making it difficult to keep fresh without major operational costs.

**7.7.2.4** **Special Note: Photoresist is not allowed in the standard pre-furnace clean SVC-14 baths for cross-contamination reasons. Staff must approve any use of SVC-14 for stripping photoresist. SVC-14 is the exception to the vigorous reaction rule above – proper use of SVC-14 to strip photoresist is possible, but the Nanolab limits standard baths to cleaning use only.**

**7.7.3** RCA1

**7.7.3.1** Ingredients: 5:1:1 $H_2O$:$NH_4OH$:$H_2O_2$

**7.7.3.2** Mechanism of cleaning: Chemical removal via caustic reaction

**7.7.3.3** Significant known issues: Actively attacks many materials, leaves oxide on surface which needs HF dip to remove.

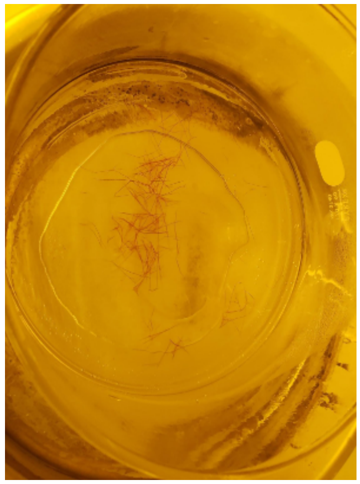
## *8.0 Process Procedure*

**8.1** Wet Photoresist Strip – Standard Baths

**8.1.1** msink1

**8.1.1.1** These baths are contamination controlled. Review msink1 manual and confirm all materials on your wafer are allowed into the bath. Consult with process staff if you have any questions.

**8.1.1.2** Wafers that have gone through a UV Bake (such as axcelis) are not allowed in the communal 1165 baths. These have been shown to cause photoresist “stringers” in the bath. If you need 1165 after going through axcelis (with any photoresist and any program) you must use your own beaker of chemical.



**8.1.2** msink2

**8.1.2.1** These baths are gold-contaminated and mobile ion-contaminated. Confirm your wafers can utilize this bath without affecting downstream process flows before using.

**8.1.3** Msink16/18

**8.1.3.1** Prepare chemical bath at msink16/18.

**8.1.3.1.1** **Solvents are never allowed to be directly heated via hot plate. Always use a water bath as an intermediary!**

**8.1.3.2** Immerse wafers in bath. Wait until photoresist is stripped (typically 30 minutes).

**8.1.4** Long Soak Process

**8.1.4.1** Some wafers require a long soak procedure, notably those which still have hardened layers on them. This is typically done over the course of 2-3 hours, and sometimes overnight.

**8.1.4.2** The films requiring long soak processes are typically also vulnerable to plasma ashing in matrix, but take 2-3 cycles.

**8.1.5** Rinse in QDR or via H2O gun depending on sink being used.

**8.1.5.1** Alternatively, some chemistries require rinse in solutions other than water. See chemistry options below.

**8.1.6** Dry in SRD or hand dry via N2 gun.

**8.2** Dry Photoresist Strip

**8.2.1** See Matrix manual for details on plasma stripping of photoresist.

**8.2.2** Note that the ptherm, technics-c, and yes-g500 all have O2 plasma and are often confused as capable of photoresist stripping. These are etching and cleaning tools, which do not rapidly remove photoresist effectively. They are not strip tools.

## *9.0* ***Troubleshooting Guidelines***

**9.1** Water bath heating

**9.1.1** Symptom: Water bath will not reach temperature / is not accurate.

**9.1.2** Solution: Use thermocouple attachments in msink16/18 to monitor actual water temperature inside bath, and actively change hot plate measurement to reach steady state. **Never walk away from a hot plate while it is ramping to temperature.**

## *10.0 <u>Figures & Schematics</u>*

### 11.0 ***Appendix A - Composition of other Photoresist Strip options***

| Product | Component 1 | Component 2 | Component 3 | Component 4 | Component 5 | Component 6 | Component 7 |
|---|---|---|---|---|---|---|---|
| PRS-1000 | Diethylene Glycol Monoethylether 10-20% | Thiophene, Tetrahydro-, 1,1-dioxide 25-45% | 1-Methyl-2-pyrrolidinone (NMP) 35-55% | Tetraethylene Glycol (1-10%) | | | |
| PRS-2000 | Tetraethylene Glycol (4-12%) | Diethylene Glycol Monoethylether 10-20% | Thiophene, Tetrahydro-, 1,1-dioxide 20-40% | 1-Methyl-2-pyrrolidinone (NMP) 30-50% | 2-Propanol, 1-amino- (5-20%) | | |
| PRS-3000 | Thiophene, Tetrahydro-, 1,1-dioxide 30-50% | 1-Methyl-2-pyrrolidinone (NMP) 40-50% | 2-Propanol, 1-amino- (5-15%) | | | | |
| PRX-127 | Dipropylene glycol monomethyl ether <30% | Dimethyl sulfoxide <75% | TMAH pentahydrate <4% | | | | |
| PRR-002 | Dipropylene Glycol Methyl Ether 10-15% | Diethylene Glycol Monobutyl Ether 10-15% | Ethylene Glycol Butyl Ether 10-15% | N-Methyl-2-Pyrollidone 40-50% | Dibutylnaphthalene Sulfonate <1% | Ethoxylated Nonylphenol 5-10% | Water 5-10% |
| PRR 5-4 | Potassium Hydroxide <1% | Sodium Hydroxide 10% | Dimethyl Sulfoxide 8% | Water 81% | | | |
| Resist Strip 586 | Sulfolane 70-74% | 2-(2-aminoethoxy)ethanol 27-29% | Surfactant <1% | | | | |
| 1165 Remover | 1-Methyl-2-pyrrolidinone (NMP) 94-95% | Pyrrolidinone Compound (5-6%) | | | | | |
| SVC-14 | Dimethyl sulfoxide <60% | cyclic ester (>40%) | | | | | |
| Remover PG | N-Methyl-2-pyrrolidinone >99% | Proprietary surfactant <1% | | | | | |