



SPM Photoresist Stripping and Cleaning

Introduction

Sulfuric acid (H₂SO₄) and hydrogen peroxide (H₂O₂) mixture (SPM) is used for various wet cleaning process steps. Some common cleaning and surface conditioning sequences that include for SPM are shown in the Table 2.1:

Cleaning Step	Chemicals	Typical Sequence
Photoresist stripping	1) H ₂ SO ₄ :H ₂ O ₂	1) SPM
Post-resist strip cleaning	2) H ₂ SO ₄ :H ₂ O ₂	2) SPM
Post-resist strip cleaning	1) H ₂ SO ₄ : H ₂ O ₂	1) SPM
Residue removal	2) NH ₄ OH:H ₂ O ₂ :H ₂ O	2) SC-1
Residue removal	1) HF: H ₂ O 2) H ₂ SO ₄ :H ₂ O ₂ 3) NH ₄ OH:H ₂ O ₂ :H ₂ O	1) DHF 2) SPM 3) SC-1
Residue removal	1) H ₂ SO ₄ :H ₂ O ₂ 2) NH ₄ OH:H ₂ O ₂ :H ₂ O 3) HF:NH ₄ F:H ₂ O	1) SPM 2) SC-1 3) NOE
Pre-oxidation cleaning	1) H ₂ SO ₄ :H ₂ O ₂ 2) HF:H ₂ O 3) NH ₄ OH:H ₂ O ₂ :H ₂ O 4) HCl:H ₂ O ₂ :H ₂ O	1) SPM 2) DHF 3) SC-1 4) SC-2

Table 1. Common processes applications using SPM.

Resist Stripping and Post-resist Stripping Clean

Resist stripping involves removal of all the photoresist applied to the wafer for the photolithography delineation step. The stripping step can occur after receiving a reactive ion etching (RIE) process, a wet etching



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process, an ion implantation process, or a metal deposition lift-off process. Positive photoresist is typically composed of a Novolac or PhOSt (phenyl oxy styrene) resin with a photoactive compound, solvents are used to make a viscous liquid, which is spun on the wafer surface, while negative photoresist is typically composed of PMMA (poly methyl methacrylate) (reference), with additives similar to the positive photoresist. These compounds are composed of hydrocarbons, with other elements present, either as part of molecules in the resin or additives, or as impurities. The impurities in photoresist can be metallic; both mobile ions and heavy metals are found in the ppm to ppb range.

Post-resist strip cleaning occurs after the plasma resist stripping step; also known as ashing or resist removal. Post-resist strip cleaning using SPM removes residual organic material, but does not remove polymeric material composed of fluorocarbons, additional wet cleaning step using other chemistry is required and will be discussed in Section 3.0.

The most common process for the photoresist removal process is most commonly a combination of plasma resist strip to remove the majority of the resist followed by a SPM wet cleaning process to remove the remaining organic residue. The plasma stripping process does have an effect on the subsequent residue remaining after the plasma exposure.

SPM chemistry formulations are limited in the capability of removing photoresist that has had various process steps performed; removing photoresist that has been implanted at a dose less than about $1.0E14$ atoms/cm² is possible, however, doses greater have required plasma stripping before the SPM step. Etching processes limit the capability of polymer removal by depositing a fluorocarbon-based layer and chemistry other than SPM is required for adequate polymer removal.

Two baths are typically used for SPM processing. The bath life of the first SPM bath is less than the second due to the amount of photoresist to be digested. Typically, the first bath is replaced at a faster rate than the second bath, or conversely, the second bath becomes the first bath when the original first bath is replaced. The bath lives are much longer for post-strip cleaning than for bulk resist strip. Interchangeability of the baths between post-strip cleaning and bulk photoresist stripping is possible, but not recommended.

Residue Removal

Residue removal usually occurs after an etching or an implantation step. Since photoresist is an organic material containing long-chain polymer, oxidation is easy and the removal of the polymer from the surface complete when no other substance is present. However, when there is residue present from previous processing, it must be removed before the wafer is sent to the next step. The difficulty of residue removal depends on the prior processing; baking of the resist hardens it by depleting the solvents, ultraviolet (UV) exposure cross-links the resist (reference), etching depletes the resist of solvents and etches the resist while depositing a polymer on the surface (reference), and ion implantation cross-links and dehydrogenates the resist yielding a "crust" near the outer surface of the resist.



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The residue must be removed, and typically in conjunction with plasma stripping of the photoresist mask. The residue contains both organic (often F-containing) and inorganic (often Si-containing) materials. For example, after the gate stack is etched, a sequence of SPM and HF is normally used for removal of both etching and stripping residues, in addition to unwanted gate oxide that remains in the etched areas, as shown in Table 1.

Pre-oxidation Cleaning

Thin layers of organic film are present on the wafers surface from atmospheric contamination found in the device fabrication area. Organic vapors can outgas from polymeric components such as wafer carriers and building materials. Although these levels of contamination are low, the processes a wafer receives are sensitive to these low levels and the surface must be cleaned prior to thermal processing, for example. In many fabrication areas, a SPM cleaning step is part of the RCA pre-thermal cleaning process.

SPM Chemistry Formulations

The most common chemistry used for front end of line (FEOL) photoresist removal and post-resist strip cleaning is SPM. The ratio of $H_2SO_4:H_2O_2$ varies, but commonly a mixture by volume of between 2:1 and 4:1 H_2SO_4 : (96wt%): H_2O_2 (30wt%), ratios as high as 8:1 have been used. In normal process procedures for preparing SPM batch, the initial ratio is mixed, and then subsequent additions of H_2O_2 are added to maintain the ratio. Section 1.0 discusses the chemicals and their properties. The SPM mixture is typically $>100^\circ C$ to assure complete reaction and to remove any remaining residues. The temperature of the solution is important; too high a temperature can cause rapid decomposition and thus depletion of the H_2O_2 , while too low a temperature causes slow removal rates of photoresist. Mixing of H_2SO_4 and H_2O_2 creates an exothermic reaction (heat is created) causing the ambient (room or storage) temperature of the solutions to rise. To maintain and regulate the temperature heat is applied to the bath, typically temperatures range from 90 to $140^\circ C$. Temperatures and volume ratios of SPM control the strip rates of photoresist. Although the exact removal rates are based on the resin and process conditions in preparation of the photoresist, the trends associated with the SPM process are consistent for all photoresist materials; higher temperatures cause faster removal rates and lower SPM ratios lead to lower removal rates. Table 2 shows the volume ration ranges and temperatures used for the SPM solution.

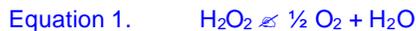
Volume Ratio $H_2SO_4:H_2O_2$			Temperature		
High	Suggested	Low	High	Suggested	Low
8:1	4:1	2:1	$140^\circ C$	$110^\circ C$	$90^\circ C$

Table 2. Typical volume ratios and temperatures used for SPM.



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The H_2O_2 in the SPM decompose rapidly, even without processing of photoresist. The H_2O_2 molecule decomposes as shown in Equation 1, yielding a byproduct of H_2O , which dilutes the bath. As the H_2O_2 decomposes, the bath needs to be replenished with fresh chemical, typically before a new batch of wafers is processed. Typical bath life for SPM operating at temperatures of $100^\circ C$ is about 4 hours before replenishment is needed. Continuous replenishment of chemicals to prevent the degradation of the cleaning ability due to depletion of H_2O_2 in the baths is accomplished by the MTS spiking system.



Hydrogen peroxide is an effective oxidizing agent and the reaction of the hydrocarbon-based photoresist and the oxidizing agent occurs spontaneous at room temperature and pressure. Equation 2.2 shows the oxidation reaction of the decomposition of the photoresist through the intermediary carboxylic acid to the final reaction products of CO_2 and H_2O .



The color change in the SPM bath can be tracked during processing, the initial color of the SPM bath has a slight yellow tinge that is transparent, after a batch a coated photoresist wafers is placed in the bath, the color of the bath turns to dark brown and is opaque. Once the photoresist is digested, the color returns to the original tinge, approximately 15 minutes after the wafers are placed in the bath. If the H_2O_2 is depleted, the color does not return to the original, and additional H_2O_2 should be added.

Post-SPM Rinsing and Drying

The viscous SPM is hard to remove off the surface of the wafer and requires extensive rinsing. Hygroscopic sulfur (S) residues on the surface can absorb moisture and create particulate defects. Effective rinsing is critical to prevent any residual chemical from remaining on the wafer surface. Rinsing is covered in this technical guide. Drying after SPM processing is dependent in the wafer surface. SPM processing of a bare Si surface creates a thin oxide layer, known as chemical oxides that are self-limiting and typically are less than 1.0-1.2nm and are not stoichiometric SiO_2 , but SiO_x . Therefore, after SPM processing the Si surface is hydrophilic and can be dried with various techniques, surface tension gradient drying is discussed in this technical guide.

Pre- and Post-SPM Processing



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After the SPM process, other chemical baths may be used to achieve the desired surface conditioning results. SC-1 (surface conditioning –1, H₂SO₄:H₂O₂:H₂O) treatment after SPM is commonly used as a clean-up step to remove thin organic layers or used for particle removal capability. SC-1 can be used in the same wet bench in dedicated baths or in a separate wet bench. SC-1 is discussed in the RCA cleaning section in this technical guide..

Prior to or after the SPM process HF-based formulation are used to remove Si-containing polymers and fluorocarbon polymers from the sidewall, especially after gate etch processing. Additionally, very small concentrations of HF are added to the SPM to alter wafer surface wetting properties, causing the chemical to effectively drain from the wafer after rinsing.

Chemical Filtration and Reprocessing

For H₂SO₄ and H₂O₂, the chemical distribution system with its filters can provide a 10-500-fold decrease in particle levels depending on the type of filters being used.

The particle count exiting the reprocessor was less than 6/mL (>0.5µm) and less than 0.007/mL (>1µm). Reprocessors are available for H₂SO₄ typically using distillation, in combination with filtration and ion exchange resins to remove contaminants from the chemical stream. The MTS H₂SO₄ reprocessor uses a vacuum distillation column to purify the H₂SO₄ after the H₂O and residual H₂O₂ have been thermally eliminated. The MTS reprocessor can fit into a chemical distribution system.

References