RCA Critical Cleaning Process

This paper was especially prepared by Werner Kern, the inventor of the RCA clean.

Introduction

The manufacturing of a silicon integrated circuit (IC) requires 500-600 process steps, depending on the specific type of device. Most steps are performed as unit processes with the complete wafers before dicing them into individual chips. Approximately 30% of the steps are cleaning operations, which indicate the importance of cleaning and surface conditioning.

The device performance, reliability and product yield of silicon circuits are critically affected by the presence of chemical contaminants and particulate impurities on the wafer or device surface. Effective techniques for cleaning silicon wafers before thermal treatments such as oxidation, after patterning by etching, after ion implantation, and before and after film deposition are therefore critically important because of the extreme sensitivity of the semiconductor surface and the nanometer sizes of the device features. As a consequence, the preparation of ultraclean in silicon wafers has become one of the key technologies in the fabrication of advanced ICs [1].

One may ask about the nature, types and origins of the impurities that must be eliminated. Contaminants on the wafer surfaces exist as adsorbed ions and elements, thin films, discrete particles, particulates (clusters of particles) and adsorbed gases. Surface contaminant films and particles can be classified as molecular compounds, ionic materials, and atomic species. Molecular compounds are mostly particles or films of condensed organic vapors from lubricants, greases, photoresists, solvent residues, organic compounds from DI (deionized) water, fingerprints or plastic storage containers and inorganic compounds. Ionic materials comprise cations and anions mostly from inorganic chemicals that may be physically adsorbed or chemically bonded (chemisorbed), such as ions of sodium, fluorine, and chlorine. Atomic or elemental species comprise metals such as copper and heavy metals that may be electrochemically plated out on the semiconductor surface from hydrofluoric acid (HF)- containing solutions, or they may consist of silicon particles, dust, fibers or metal debris from equipment.

Particles can originate from airborne dust from equipment, processing chemicals, factor operators, gas piping, wafer handling and film deposition systems. Mechanical (moving) equipment and containers for liquids are especially prolific sources, whereas solid materials, liquids, gases, chemicals and ambient air tend to cause less particle contamination, but all can contribute significantly to the generation of chemical impurities.

The objective of wafer cleaning and surface conditioning is the removal of particles and chemical impurities from the semiconductor surface without damaging or deleteriously altering the substrate surface. The surface of the wafer must not be affected in such a manner that roughness, pitting, or corrosion negates the results of the cleaning

process. Plasma, dry-physical, wet-chemical, vapor phase and supercritical fluid methods can be used to achieve these objectives. However, the most widely used and traditional approach of wafer cleaning and surface conditioning prior to the formation of metal conductor lines is based on aqueous-chemical processes that typically use hydrogen peroxide mixtures. Successful results have been achieved by this approach for the past twenty-five years.

The best-known system of this type is known as the "RCA cleaning process," which will be described in this paper. It is used for cleaning silicon wafers in the initial stages of processing. These wafers feature only single-crystal or polycrystalline silicon with or without silicon dioxide and silicon nitride layers or patterns, without exposed metal areas. Reactive chemicals with aqueous solutions can be used for cleaning and conditioning these corrosion-resistant materials. Cleaning at the early stages is typically done prior to gate oxide deposition and high-temperature processing, such as thermal oxidation and diffusion. The elimination on contaminants before these process steps is especially critical to prevent impurity diffusion into the substrate materials.

Cleaning wafers in the "Back End Of Line" (BEOL), which is later on in the processing, is much more restrictive because metal areas may be exposed such as copper, aluminum, or tungsten metallization, possibly in conjunction with low-density or porous low-k dielectric films. Dry cleaning methods based on plasma-assisted chemistry, chemical vapor phase reactions, and cryogenic aerosol techniques can be used to remove organic resides and particulate contaminants. Aqueous/organic solvent mixtures and other innovative approaches may also be used that will not attack exposed sensitive materials.

The discussion of the RCA cleaning process will include the following processing sequence:

1) Preliminary Cleaning
2) RCA Cleaning
3) Standard Clean- 1 (SC-1)
4) Standard Clean- 2 (SC-2)
5) Modifications to SC-1/SC-2
6) HF-Last

Preliminary Cleaning

The removal of gross impurities, including photoresist masks after patterning can be accomplished by either dry or liquid methods. Reactive plasma-assisted cleaning usually using oxygen-based plasma is the most widely employed dry method, which has been used routinely in the IC manufacturing for many years [2]. Several types of plasma sources are commercially available. Ion-induced damage to the substrate device wafers has been a concern but can be controlled to some extent.

Liquid-phase processing is often used to complete the plasma ashing step or may be used instead of it entirely. It is based on immersing the wafers in mixtures of 98% H_2SO_4 and 30% H_2O_2. Volume ratios of 2:1 to 4:1 are used at a temperature of 100-130°C for 10-15 min. Organics are destroyed and eliminated by wet-chemical

oxidation, but inorganic contaminants such as metals are not desorbed. The silicon surface after this cleaning step is strongly contaminated with sulfur residues from the sulfuric acid [3]. These "sulfuric-peroxide mixtures" (SPM), which are also known as "piranha etch" (because of their voracious ability to eradicate organics) are dangerous to handle in the fab; goggles, face shields, and plastic gloves are needed to protect the operators. Vigorous rinsing with DI water is required to completely remove the viscous liquid. Finally, it is advantageous after the water rinsing step to strip the impurity-containing formed oxide film on bare silicon by dipping the wafers for 15 sec in dilute hydrofluoric acid, HF-H_2O (1:50), followed by a DI water rinse. A modification an be made by adding minute amounts of HF to the SPM which results in repellency, better sulfur removal, shorter rinsing times, and improved particle elimination [3].

RCA Cleaning

The first successful process for wet-cleaning silicon wafers prior to metallization was systematically developed at RCA, used for several years in their fabs, and finally published in 1970 [4]. The process consists of two consecutively applied hot solutions known as "RCA Standard Clean", SC-1 and SC-2, featuring pure and volatile reagents. These solutions have been widely used in their original or modified form for over forty years in the fabrication of silicon semiconductor devices. The SC-1 solution for the first processing step consists of a mixture of water (H_2O), hydrogen peroxide (H_2O_2), and ammonium hydroxide (NH_4OH); it is also known as "APM" for "Ammonia/Peroxide Mixture". The SC-2 solution for the second processing step consists of a mixture of water, hydrogen peroxide, and hydrochloric acid (HCl); is also known as "HPM" for "Hydrochloric/Peroxide Mixture". Both treatments leave the silicon surface after water rinsing with a thin hydrophilic oxide layer.

Standard Clean- 1

The originally specified composition for SC-1 solution ranges from 5:1:1 to 7:2:1 parts by volume of H_2O, H_2O_2, and NH_4OH. The ratio usually used is 5:1;1. DI (deionized) water is used for all operations. The hydrogen peroxide is electronic-grade 30% H_2O_2, unstabilized (to exclude contaminating stabilizers). The ammonium hydroxide is 29% NH4OH. Treatment of the wafers can range from 5 to 10 min at 70-75°C followed by a quench and overflow rinse in running DI water. Diluting the hot bath solution with cold water is done to displace the surface level of the liquid, and to reduce the bath temperature to prevent any drying of the wafer batch upon withdrawal from the bath. The batch of wafers is rinsed in cold running DI water and then transferred into the SC-2 bath. The SC-1 solution was designed to remove from silicon, oxide, and quartz surfaces organic contaminants that are attacked by both the solvating action of the ammonium hydroxide and the powerful oxidizing action of the alkaline hydrogen peroxide. The ammonium hydroxide also serves to remove by complexing some periodic group IB and IIB metals such as Cu, Au, Ag, Zn, and Cd, as well as some elements from other groups such as Ni, Co, and Cr. Actually, Cu, Ni, Co, and Zn are known to form amine complexes. It was not originally realized that prior to the ability to perform

AFM (atomic force microscope) analysis, SC-1 dissolves the thin native oxide layer on silicon at a very low rate and forms a new oxide on the silicon surface by oxidation at approximately the same rate. This oxide regeneration is now believed to be an important factor in the removal of particles and chemical impurities on as well as in the silicon surface.

It is important to realize that the thermal stability of SC-1 is very poor especially at elevated temperature under treatment conditions. The H_2O_2 decomposes to water and oxygen and the NH_4OH looses NH_3 by evaporation. Mixtures should therefore by freshly prepared before use for best results. Vessels of fused quartz (silica) must be used to contain the bath solutions rather than Pyrex glass to avoid contamination from leached components.

Standard Clean- 2

The originally specified composition for the SC-2 composition ranges from 6:1:1 to 8:2:1 parts by volume of H_2O, H_2O_2, and HCl. The ratio usually used is 5:1:1, for simplicity. The water and hydrogen peroxide are as noted above for SC-1. The HCl concentration is 37wt%. The treatment of the wafers can range as for SC-1: 5 to 10 min at 70-75°C followed by a quench and overflow rinse. The wafers are rinsed in cold running DI water and then dried. They are immediately transferred to a glass or metal enclosure flushed with pre-filtered nitrogen for storage if they cannot be processed immediately.

The SC-2 solution was designed to dissolve and remove from the silicon surface alkali residues and any residual trace metals such as Au and Ag, as well as metal hydroxides including $Al(OH)_3$, $Fe(OH)_3$, $Mg(OH)_2$, and $Zn(OH)_2$. Displacement replating from solution is prevented by formation of soluble metal complexes with the dissolved ions. The solution does not etch silicon or oxides and does not have the beneficial surfactant activity of SC-1 for removing particles. SC-2 has better thermal stability than SC-1 so that the treatment temperature and bath life does not need to be as closely controlled.

Modifications to SC-1/SC-2

Several improvements to the original RCA cleaning procedure were reported by Kern in a number of papers [5-8]. The most influential of these changes was the introduction of the RCA megasonic cleaning system for the cleaning and rinsing of wafers [7]. Megasoinic treatment is especially advantageous for physically dislodging from the wafer surface particles in SC-1 cleaning due to the high level of kinetic energy. It allows a substantial reduction in solution temperature and offers a much more efficient mode of rinsing than simple immersion tank processing.

No gross etching of silicon or oxide was shown to occur with SC-1 even if the hydrogen peroxide concentration is reduced by a factor of 10. Finally, an optional process step was introduced by stripping the hydrous oxide film formed after SC-1 with high-purity particle-free, 1:50 HF for 10 sec so as to re-expose the silicon surface for the subsequent SC-2 treatment.

The development of several improvements in RCA cleaning have been reported in the early literature and relate mainly to these areas of processing:

1.) Reduction of the NH_4OH concentration in SC-1 by at least four-fold to prevent micro-roughening of the silicon surface and to enhance particle removal, thereby improving the quality of gate oxides (9)(10). A typical composition can be 5:1:0.25 (H_2O:H_2O_2:NH_4OH).

2.) Dilution of SC-1 and SC-2 with DI water to various concentrations while still achieving good cleaning effectiveness (11). Dilutions of 10 are typical.

3.) Replacement of SC-2 with very dilute room temperature HCl is possible since Au and Ag contaminants are now no longer present in high-purity process chemicals. Previously any deposits of Au or Ag on silicon required SC-2 for oxidative desorption. Other residual metals and their hydroxides are readily soluble in dilute HCl (12).

HF Last

"HF-Last" processing is used for creating an oxide-free, hydrogen-passivated, hydrophobic silicon surface by briefly immersing SC-1/SC-2 cleaned hydrophilic wafers as a last step of the RCA cleaning sequence in very dilute (1:100) ultrahigh-purity HF, followed by final rinsing and drying (13-15). Alternatively to this wet-processing, the wafers can be expos ed to HF-IPA (isopropyl alcohol) vapor (14). In either case, a very clean hydrogen-passivated, hydrophobic silicon surface results which is suitable for the epitaxial growth of silicon layers where no oxide traces can be tolerated.

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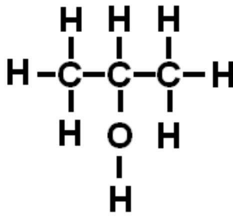
APPENDIX A

Chemical Properties



Isopropyl alcohol

- IUPAC nomenclature: 2-propanol
- CAS No: 67-63-0
- Chemical formula: C_3H_8O
- Molecular weight:: 60.09 g/mole
- Vapor pressure: 33 mm at 20°C, 44 mm at 25°C
- Specific gravity: 0.79 g/ml
- Surface tension: ~30 mN/m (~72 mN/m for H_2O)
- Critical temperatures
  - Boiling point 82-106°C
  - Flash point: 12-35°C (depending on reference)
  - Melting point -89°C
- MSDS
  - Health: 1; Flammability: 3; Reactivity: 0
  - Low toxicity
  - Skin irritant
  - Highly flammable

Chemical Usage

Typical IPA usage

- POR 5 ml/min
  - Range 5 ml/min to 15 ml/min
  - Tank with vapor pressure ~5 to 7 ml depending on cassettes
- POR 60 sec
- Range 60 sec to 180 sec
- Specification for disposal: San Jose
  - Limits on toxic organics <10µg/L
  - Limit on disposal of pure organics with flash points <60°C
    - No spec found on allowable IPA in water disposal limits (request for information in progress)