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Wet Cleaning Technology –Chemistry

Jerzy Ruzyllo, Penn State University

As indicated in SN-15 "*Cleaning in Semiconductor Device Manufacturing"* wet cleaning is the dominant cleaning technology in semiconductor device manufacturing. Wet cleans use combinations of acids, solvents, surfactants and deionized water to dissolve, oxidize, etch, and scrub contaminants from the wafer surface. An integral part of every wet cleaning scheme are rinses in ultra-pure deionized (DI) water, often heated to increase rinse efficiency and often with ozone added (DIW/O_3). Its role is to stop chemical reaction(s) on the wafer surface and to wash reactants and reaction products off the surface. Wet cleaning sequence is always completed with a carefully executed wafer drying process.

Wet cleaning recipes vary depending on application and the extent of surface contamination. In general however, they draw from the pool of chemical mixtures that were first proposed over 30 years ago as the so-called RCA clean [1] and since then were significantly modified. The sequence shown below represents a complete cleaning process (e.g. pre-gate oxidation) which was designed to remove from the surface heavy organics, particles, metallic contaminants as well as to control native/chemical oxide

Chemical Clean Step 1 – The purpose of this step is to remove organic contamination remaining on the surface following resist stripping. The H_2SO_4:H_2O_2 solution at 100°C-130°C, also known as **SPM** (Sulfuric Peroxide Mixture), or "piranha" clean, or "CARO" clean is used. More recently, it is often replaced with a Sulfuric acid/Ozone Mixture (**SOM**).
Chemical Clean Step 2 – Native/chemical oxide etch using diluted HF:H_2O (**DHF**) solution at the ratio of 1:100 or weaker.
Chemical Clean Step 3 – The prime objective of this step is to remove particles from the surface along with light organic contaminants. Almost uniquely it involves NH_4OH : H_2O_2 : H_2O mixture (Ammonium hydroxide-hydrogen Peroxide Mixture, or **APM**) also known as SC1 (Standard Clean 1) or RCA 1. Recently, weak solutions, e.g. 1:1:50, at temperature < 70°C are used, typically in conjunction with megasonic agitation.
Chemical Clean Step 4 – This step is specifically addressing an issue of metallic contamination. It uses HCl: H_2O_2 : H_2O mixture (Hydrochloric acid – hydrogen Peroxide-water Mixture, or **HPM**) also known as also known as SC1 (Standard Clean 1) or RCA 1. Dilution and bath temperature are similar to APM. As opposed to APM, however, this step is rarely used in advanced cleaning applications.

The above sequence is very resources and time consuming and in practice it is simplified in a variety of ways. Significantly improved understanding of cleaning processes as well as much improved overall cleanliness of semiconductor manufacturing resulted in substantially relaxed requirements regarding strength and complexity of cleaning chemistries. Besides, due to the fragility of ultra-thin films and deep sub-100 nm structures in state-of-the-art devices, and due to the need to prevent any material losses during cleaning, less aggressive cleans are used to prevent excessive chemical attack. As a result, wet cleaning chemistries are being significantly modified. Currently, in many applications a sequence involving just one cleaning step followed with D.I. water rinse and dry is sufficient.

An example of such simplified, yet effective sequence would be the process ("IMEC-ozone" clean) in which "clean" would comprise of an ozone/water (O_3/H_20, ozonated water) exposure followed (without a rinse) with treatment in a very weak solution of HF:HCl:H_2O (e.g. 0.025:1:5) and completed with a rinse/dry cycle.

[1]. W. Kern and D. Poutinen, RCA Rev., 31, 187 (1970)