A Study of Metallic Contamination Removal and Addition using Modified SC-1 Solutions

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The RCA clean is widely used in the semiconductor industry during various wet-chemical cleaning processes. The RCA clean consists of a particle removal step, the Standard Clean 1 or SC-1 step and a metallic impurity removal step, the Standard Clean 2 or SC-2 step. In this work, we have investigated the addition of chelating agents in SC-1 solutions to (i) prevent metallic deposition and (ii) remove metallic impurities during the SC-1 step, resulting in a very fast RCA replacement clean, opening the door for single wafer wet cleaning.

Although SC-1, a mixture of $NH_4OH/H_2O_2/H_2O$, is an efficient particle removal solution, it inherently allows some metallic impurities in solution to deposit on the wafer surface [1]. In aqueous solutions, such as SC-1, a silicon wafer surface is hydroxide terminated (hydrophilic). The interaction of the metal ions in solution and the silanol surface groups can be described by a surface ion exchange mechanism represented by the following equation:

$$\text{-Si-O-H} + M^{x+} \Leftrightarrow \text{-Si-O-}M^{(x-1)+} + H^{+} \qquad (1)$$

Where M^{x+} is the metallic ion. From equation 1, we can see that in SC-1 metal ions in solution tend deposit on the wafer surface (under conditions of high pH: low $[H^+]$). The pH dependence of the adsorption for most metals clearly follow this trend and deposit in SC-1 solutions (Al, Fe, and Zn deposit most readily) [1]. Equation 1 also indicates that decreasing the free metal ions in solution will tend to remove metallic contamination from the wafer surface (lower $[M^{x+}]$).

The addition of an appropriately chosen chelating agent clearly reduces metallic ion deposition in SC-1 solutions (Figure 1). For short processing times the metal removal efficiency of Fe for modified SC-1 solutions is a function of chelating agent concentration (Figure 2) and temperature (not shown). The removal of Al, known to be partially included into the chemically grown oxide [2], was shown to be a function time (Figure 2,3). Incorporation of a short dilute HF (DHF) step after the modified SC-1 step effectively to removed Al for short processing times. TOF-SIMS measurements were also carried out to confirm the absence of chelating agents on the processed wafers [3].

References:

[1] H. Hiratsuka *et al.*, Ultra Clean Tech. Vol. 3, No 3 (1991) p. 18.

[2] M. Tsuju *et al.*, ECS Proceedings, (1995) p. 316

[3] C. Beaudry *et. al.*, SPWCC Proceedings, (2001) p. 345.

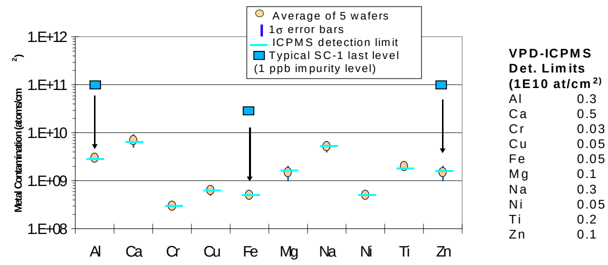

Figure 1. Metal Deposition – Surface trace metal level after modified SC-1 clean (single wafer cleaning for 30s @ 80°C).

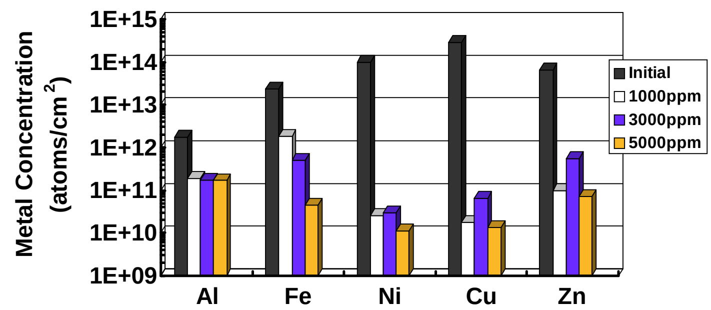

Figure 2. Metal Removal – Surface trace metal level after modified SC-1 clean for different concentrations of chelating agent (immersion clean for 30s @ 80°C).

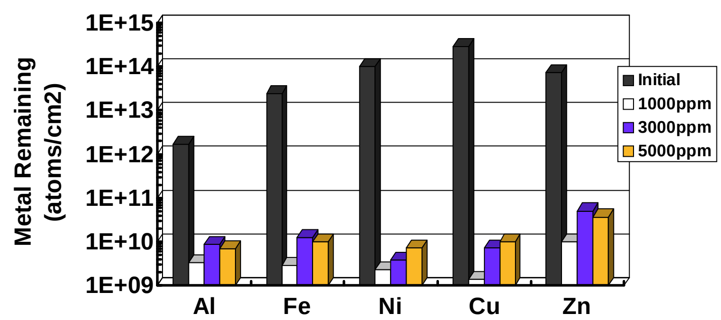

Figure 3. Metal Removal – Surface trace metal level after modified SC-1 clean for different concentrations of chelating agent (immersion clean for 10min @ 80°C).

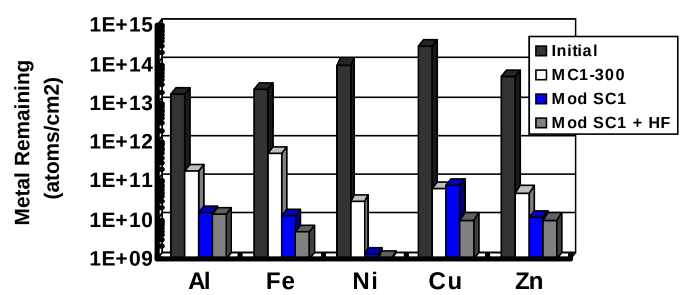

Figure 4. Metal Removal – Surface trace metal level after modified SC-1 clean, HF, and modified SC-1 + HF (single wafer clean for 60s @ 80°C).