ACTIVITY OF HF SOLUTIONS AND PARTICLE REMOVAL USING HF SOLUTIONS

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It has been published that the active species in HF solution are HF, HF_2^-, F^-, and H_2F_2 (1). The dissociation constants for these species at 25 degrees Celsius are:

$[H^+][F^-]/[HF] = 6.85 \times 10^{-4}$

$[HF_2^-]/[HF][F^-] = 3.963$

$[H_2F_2]/[HF]^2 = 2.7$

It has also been found that the HF_2^- and H_2F_2 species are responsible for etching silicon dioxide (2). These papers have assumed that the activity coefficients for the species in HF solutions are unity. We have used the extended Debye-Huckel equation (eq. 1) to calculate the activity coefficients (γ) for ionic strengths less than 0.1 mol/liter. For higher ionic strength solutions we have used the Davis equation (eq.2).

$$\gamma = 10\wedge\left(\frac{-0.512\, z^2\, \sqrt{\mu}}{1+100r\sqrt{\mu}/305}\right) \qquad \text{Eq. 1}$$

$$\gamma = 10\wedge\left(\frac{-0.512\, z^2\, \sqrt{\mu}}{1+\sqrt{\mu}-0.2\mu}\right) \qquad \text{Eq. 2}$$

Were z is the ionic change, μ is the ionic strength in mol/liter, and r is the hydrated radius of the ion in Angstroms.

The effect of including activity coefficients on the concentration of species in solution, the pH of the solution, and amount of pH adjustment chemical to add will be discussed. Dilute HF solutions that have been buffered with HCl , NH_4F, or NH_4OH or are unbuffered will be discussed.

The prevention of particle deposition has been reported to be dependent on pH and ionic strength in HF solution (3). We hypothesize that conversely the particle removal efficiency in HF solutions depends on the pH and ionic strength. Certainly in order to have high particle removal efficiency one must minimize particle re-attachment.

From the activity coefficients we calculate the amount of HCl or NH_4OH to mix with HF to get the desired pH at various HF concentrations. We use these pH adjusted HF solutions to remove Si_3N_4, Si, SiO_2, and W particles from Si and SiO_2 substrates. Correlation of the particle removal efficiency with species concentration, time, amount of oxide etched, and solution pH and ionic strength will be reported for the various particle and substrate combinations.

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3) D. M. Knotter, Y. Dumesnil, In Ultra Clean Processing of Silicon Surfaces, M. Heyns, P. Mertens, and M. Meuris, Editors, Solid State Phenomena, Vol. 76-77, pg. 255 (2001).