Prevention of Si Etching in Diluted SC1 Solutions

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Very diluted SC1 solutions at low concentrations (1:1:50 or more) are used to maintain reasonable chemical consumption in single tank or single wafer tools. In these conditions SC1 behaves differently from conventional high concentration chemistries used in re-circulated systems, and severe defectivity and electrical issues may arise[1], especially if temperature is above 50-60°C.

These issues are related to excess silicon etching and COPs revealing in the silicon substrate. K.Yamamoto et al. explained this phenomenon[2], showing that in case of low H_2O_2 concentration mixtures, such as diluted solutions, NH_3 etches directly the silicon diffusing through the native oxide layer. This kind of reaction has a much higher Si etch rate than the oxidation-etching reaction by OH-.

Etching of silicon surface is a very challenging measurement, because it cannot be made using the conventional optical methods, without SOI substrates. Anyway, a good approximation can be obtained using amorphous silicon (α-Si) on an oxidised substrate and measuring the α-Si thickness by spectroscopic ellipsometry, using a three-layer model.

A design of experiment was performed to evaluate the amount of silicon etched as a function of chemical concentration, bath temperature and dip time, for both SC1 and HF-SC1. In case of SC1 the amount of etched thermal oxide has been also evaluated. Experiments were carried on a DNS FC821L wet station, using an ONB tank. In this tool chemicals are injected into the bath for 120", than wafers are dipped in a static solution and in-situ rinsed. During the dip the bath temperature slightly decreases, because the quartz tank is not heated.

Figure 1 shows the amount of α-Si and SiO_2 etched at 50°C as a function of dipping time. The 0 value on the x-axis refer to 120" chemical injection only. In case of HF treated surfaces silicon has no protection and during the injection time about 8Å of α-Si are removed. SC1 and HF-SC1 curve are then parallel, and therefore the etching rate is the same.

To protect Si from etching it has been introduced an oxidising step after before SC1 or between HF and SC1. In this study two solutions have been considered, diluted peroxide at high temperature and DIW/O_3. As shown in Figure 2, ozonised water is much more efficient than diluted peroxide to oxidise silicon.

Figure 3 shows the amount of amorphous silicon removed by a conventional 1:2:20 SC1 and by 1:2:100 diluted SC1 after HF etching. The ozone injection prevents α-Si etching and the total amount of etched silicon is lower than the one obtained by 1:2:20 SC1, even at higher SC1 temperature. A similar behaviour can be found for SC1 without any HF step.

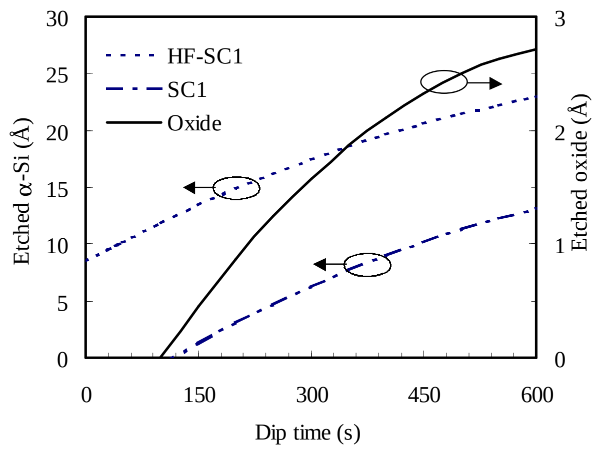

Figure 1: α-Si and SiO_2 etching by HF-SC1 and SC1

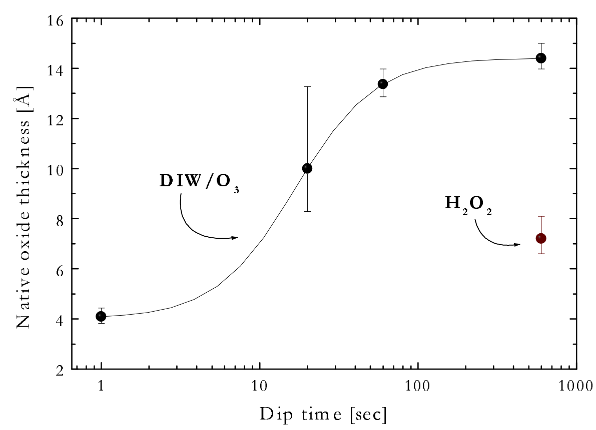

Figure 2: Native oxide re-growth by 15ppm DIW/O_3 and H_2O_2 (1:50, 50°C)

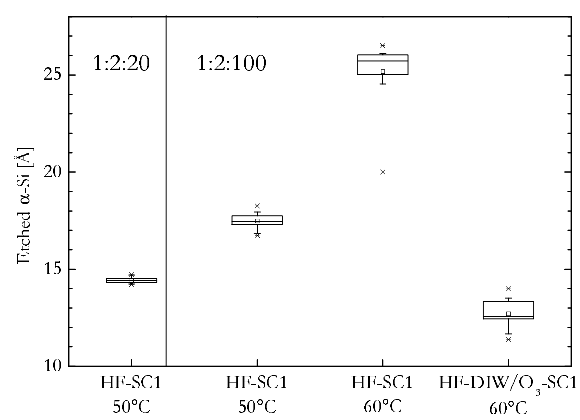

Figure 3: α-Si etching by HF-SC1 for conventional (left) and diluted chemistries (right).

[1] S.Petitdidier, H.Bernard, E.Bellandi, F.Landa, H.Shirakawa, D.Levy, Proceedings of the 5th UCPSS, Oostend, Be, September 2000

[2] K.Yamamoto, A.Nakamura and U.Hase, IEEE transactions on semiconductor manufacturing, Vol. 12, No.3, August 1999