Effect of H_2O_2 and IPA Addition in Dilute HF Solutions on Surface Etching and Particle Removal Efficiency

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The dilute HF (DHF) last cleaning has been widely used for the removal of native or chemical oxide on silicon wafer surface grown during wet treatment, especially before gate oxide growth [1]. Even though it is reported that metal ion contamination such as copper, occur during DHF treatment [2], there has been another active research on DHF and mixture of HF and H_2O_2 chemicals to remove the native oxide and metallic impurities included in native oxide [3]. The addition of surfactant [4] or alcohol [5] in dilute HF solution has been also studied to decrease the surface microroughness and reduce the particle contamination.

There has been studies on HF mixtures with IPA or H_2O_2, however no extensive studies on the mixture of HF, IPA and H_2O_2. In this study, we report the effect of addition of isopropyl alcohol (IPA) and hydrogen peroxide on etch dynamics of silicon dioxide and silicon wafer. Wafer surfaces were characterized by AFM and contact angle analyzer after the treatment in these solutions. The removal efficiency of particles and metal ions on Si and oxide wafers was evaluated in HF solution with H_2O_2 and IPA.

Wafers were cleaned in a 4:1 mixture of H_2SO_4 and H_2O_2 for 10 min and followed by 0.5% HF dipping in order to remove native oxide layer on wafer surface. The semiconductor fabrication grade chemicals, NH_4OH (28 wt% NH_3), H_2SO_4 (98 wt%), HF (49 wt%), IPA (99 wt %) and H_2O_2 (32 wt%), were used for the experiments.

The etch rates of silicon wafers in cleaning solutions were measured by analyzing the silicon concentrations in the solutions using a Inductively Coupled Plasma Mass Spectrometer (ICP-MS). The silicon wafers were immersed in 100 ml of various HF solutions for 1hr. The etch rates of silicon dioxide were measured by the Nanospec AFT 200 of Nanometrics. For the evaluation of the particle removal efficiency, alumina and silica particles were deposited on silicon wafers. The efficiency of particle removal was evaluated by Tencor 5500 Surfscan with and without the addition of IPA. Metallic contamination removal tests were also performed .

In HF solution, HF dissociates into H^+ and F^- and F^- combines with undissociated HF to form HF_2^-. The concentration of HF_2^- is dominant etching species of thermal oxide. As shown in Figure 1, the etch rate of SiO_2 was linearly increased when H_2O_2 was added in HF solution. It should be noted that the etch rate of SiO_2 in HF solution increased from 22.58 Å/min to 30.62 Å/min at 20 wt% H_2O_2. The mechanism of the increase of etch rate when hydrogen peroxide was added in HF solution is not yet understood clearly. However it mighty be possible that the addition of H_2O_2 helps to form a reaction product, H_2SiF_6, which etches silicon dioxide.

It was reported that the etch rate of SiO_2 in HF/IPA solution was smaller than that of HF solution due to the lower relative dielectric constants of IPA [4]. In the case of HF-H_2O_2-IPA solution, the effect of H_2O_2 addition on etch rate was diminished and the etch rates were very similar with those of HF solutions only containing IPA as shown in Fig. 2. These results showed that the etch rates of oxide were dependent on IPA concentration in DHF solutions.

As shown in Fig. 3, the contact angle of silicon wafer conditioned in HF-H_2O_2 solution was 73.6° without DI water rinsing. When IPA was added in HF solution, the contact angle was increased to 82.5°. In the case of HF-H_2O_2-IPA, the contact angle was measured to be ~77° and it was higher than that in HF-H_2O_2 solution. Also, IPA was often used for the improvement of particle removal due to the lower surface tension and vapor pressure. In this study, we evaluated the efficiency of particle removal with alumina and silica particles with and without the addition of IPA.

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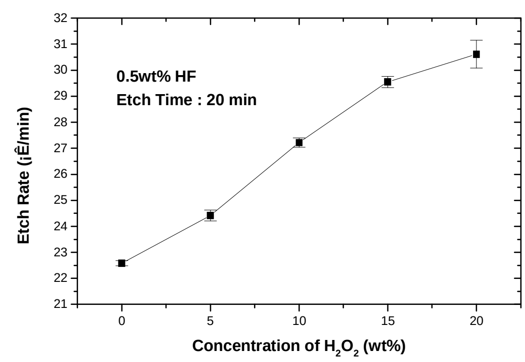

Figure 1. The etch rate of SiO_2 in HF solutions as a function of H_2O_2 concentration

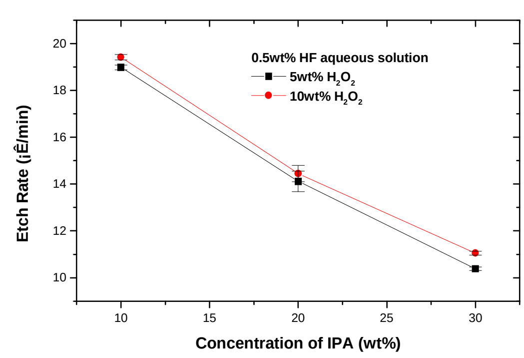

Figure 2. The etch rate of SiO_2 in HF solutions as a function of IPA concentration at 5 and 10 wt% H_2O_2

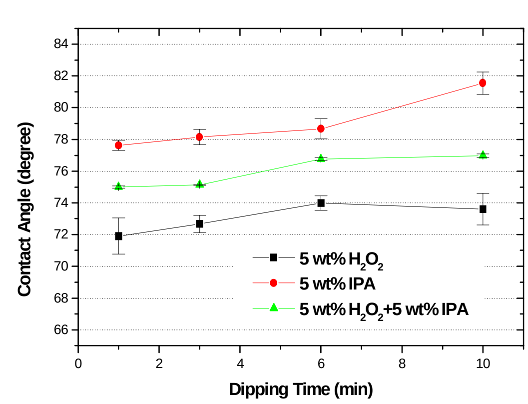

Figure 3. The change of contact angles as a function of dipping time in HF-H_2O_2, HF-IPA and HF-H_2O_2-IPA solutions