The Selective Oxidation of Si(100) Versus W
By H_2O In Hydrogen

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The selective oxidation (SELOX) of Si versus tungsten (W) is an important process to repair silicon oxide damage caused by ion implantation or reactive ion etching (RIE) around W gate electrodes on SiO_2 dielectric in the advanced CMOS devices (see Figure). The SELOX was studied using a small quartz reactor, a catalytic water vapor generator (WVG), a quadrupole mass spectrometer (QMS), an ellipsometer and a 4-point probe. New kinetics data were obtained for the wet SiO_2 growth on Si(100) at 1 atmosphere and 950-1100°C, with the steam (H_2O) in H_2 percentage being 0 to 80%. A Si(100) or a $W/SiO_2/Si(100)$ wafer was rapidly heated to a desired temperature while fast gas sequence was carried out to expose the wafer to (1) H_2 for preheating, (2) steam plus H_2 for Si oxidation and (3) H_2 or argon (Ar) for cooling. Gases in the reactor were analyzed with the QMS. The SiO_2 thickness was measured with the ellipsometer while the W film was characterized by its sheet resistance change, Auger electron spectroscopy (AES) and high resolution X-ray photo-emission spectroscopy (XPS).

Preliminary Si(100) wafer oxidation results showed that SiO_2 thickness is proportional to steam percentage at a given set of oxidation temperature and time, suggesting that the SiO_2 growth follows the first-order kinetics. At a 20% steam percentage, the SiO_2 growth rates at 969°C, 1012°C, 1056°C and 1100°C have been determined to be 0.53 Å/sec, 0.99 Å/sec, 1.85 Å/sec and 3.14 Å/sec, respectively. This yields an activation energy of 2.06 eV, in perfect agreement with the published values using O_2 or steam+O_2. Since the oxide thickness is linear with respect to the growth time, the earlier oxidation stage is kinetically controlled by an interface reaction step rather than a diffusion step. The oxidation rate equation has been determined to be:

$$R_{ox} = 2.16 \times 10^{10} \cdot \frac{1}{\sqrt{T}} \cdot e^{-\frac{E_a}{kT}} \cdot P_{H_2O} \quad (\mathring{A}\ s^{-1})$$

Where R_{ox} is SiO_2 film growth rate (Å/s), P_{H2O} is H_2O partial pressure (atmosphere), T is surface temperature (K), k is the Boltzmann constant (8.618×10^{-5} eV), and E_a is the activation energy (2.06 eV).

In addition, systematic experiments have been carried out for tungsten (W) protection in H_2O steam diluted with hydrogen (H_2) during the oxidation of Si(100) surface. Our 4-point probe data show that the sheet resistance of 500Å W/1000Å SiO_2/Si(100) wafer decreases after annealing in hydrogen and between 950°C and 1100°C. When the percentage of the steam was less than 25%, no significant increase in sheet resistance was observed. However, dramatic increase in sheet resistance occurred when 500Å W/1000Å SiO_2/Si(100) wafers were processed in >25% steam plus hydrogen and in the temperature range from 950°C to 1100°C. Thus, the selectivity window for the oxidation of Si(100) in the presence of tungsten (W) was determined to be $0<H_2O\%(\text{in } H_2)<25\%$. According to Auger electron spectroscopic (AES) depth profiles, oxygen percentages in tungsten films slightly increase after processing in steam and hydrogen mixtures within the selectivity window and between 950°C and 1100°C although the sheet resistances of the W films decrease relative to their original values. High-resolution $W(4f_{5/2,7/2})$ XPS peak analysis revealed that 91.5% W is in metal form while 9.5% W is in WO_3 form after a selective oxidation cycle. Changes in sheet resistance have been explained qualitatively in terms of electron scattering by impurities, grain boundaries and structure defects. When W films were oxidized out of the selectivity window for steam percentage (0-25%), both the oxidation of tungsten and the diffusion of silicon (Si) from the SiO_2 layers into the W layers were observed in AES depth profiles.

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