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Surface Composition Analysis of HF Vapor Cleaned Silicon by X Ray Photoelectron Spectroscopy

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XPS measurements on silicon surfaces treated by HF gaseous cleaning are described. The ratio of the SiF to OSiF concentrations is a significant signature of the desoxidation state of the surface. Hydrophobicity of the wafer appears in the range of 25 % Si-F bonds. With very agressive etching processes, 66 % Si-F bonds and 33 % O-Si-F bonds are reached and the total amount of fluorine drops below 0.3 ML. For comparison, only Si-F bonds are observed after a wet etching in a dilute HF bath without a rinse with a very lower fluorine concentration. The balance between Si-F and O-Si-F remains stable and seems to be representative of the surface states provided by the etching process.

In IC development and manufacturing silicon wafers are generally cleaned via the use of liquid reagents. Prior to device fabrication, several wet cleaning steps are performed. This so called RCA clean is intended to remove organic as well as metallic contaminants from the wafer surface and leaves behind a protective oxide of typically 4-6 monolayers thick. As a final wet treatment, just prior to insert of the wafers into processing equipment, this protective oxide is etched away by a 30-60 seconds dip in diluted HF, followed by a rinse and dry step.

There is growing interest for alternatives for wet chemical wafer pre-cleaning methods : incomplete cleaning in high aspect ratio features as a result of surface tension effects and bubbles and particulate generation may impose a process limiting factor for some process steps in ULSI fabrication.

Cleaning techniques based on gaseous reagents are a promising alternative to wet chemical cleaning. More specifically, thin protective oxides can be etched by a mixture of H_2O and HF vapour, whereby the gas species produced (SiF_4 and H_2O) are gaseous as well and can thus be transported away from the wafer surface. Also, the ability to integrate this technique with other processing steps in cluster tools is a driver behind the development of gaseous HF cleaning.

In the evaluation of the applicability of gaseous HF precleaning as an alternative to wet HF cleaning, a key point to be considered is that the silicon surface composition after a gaseous cleaning step has to be suitable for further processing. As an example, it is well known in the case of oxidation that different preoxidation cleaning procedures yield different oxidation kinetics as well as different thermal oxide properties. A detailed

understanding of the silicon surface chemistry is required to be able to determine the applicability of the HF gaseous cleaning technique as a production worthy process.

In the present paper XPS measurements are described on silicon surfaces treated by HF gaseous cleaning. Various cleaning recipes, which essentially differ by the amount of water present during the etch reaction, have been utilized and the composition of the silicon surface has been measured in terms of monolayer coverage of oxygen, fluorine and carbon.

Photoelectron spectra were obtained with MgKα radiation, the electron analyzer operated at a pass energy of 20 eV giving an overall resolution of 1.1 eV. The binding energy scale was calibrated with Au and Cu references samples 83.9 eV for Au (4f7/2) ; 932.3 eV for Cu ($2p_{3/2}$)) to determine the best analyze angle θ, the evolution of the contamination of a sample left three hours in the air was studied. An increase in carbone contamination and a decrease of fluorine content was observed, so it was better not to premote the surface and to take θ = 90°.
Si(2p), C(1s), O(1s) and F(1s) photoelectron lines were monitored and quantitative analyses were performed on these lines.
When the concentration of contaminants is low it is justified to neglect the absorption of the substrate signal through the overlayer. XPS results will then be quantified by following the submonolayer theory of Madey and Tates[1] modified by Carley and Roberts[2] .

The asymmetric shape of the C(1s), F(1s) and Si(2p) lines suggest that they are composed of several peaks.
C(1s) was fitted with two or three gaussian-Lorentzian peaks corresponding to aliphatic hydrocarbons C1 and to carbonyl and carboxyl groups C2 and C3.

F(1s) photoelectron lines were seen to be the superposition of two components which can be unambiguously related to O-Si-F and to Si-F bonds. Si(2p) photoelectron lines would be decomposed into five components depending on the oxidation state of the sample. But this decomposition was not systematically used because the difficulty to distinct Si-O bond from Si-F bond or O-Si-F bond. No simulation was done on O(1s) line.

The results obtained after gaseous etching are classified into three groups :

1) - fully deglazed samples for which the Si concentration C(Si) > 90 % ;
2) - not fully deglazed samples : 80 % < C(Si) < 90 % ;
3) - not deglazed samples : C(Si) < 80 %.

For the interpretation of the XPS results, it was kept in mind that a test for a good cleaning procedure consists in measuring the wetting angles (hydrophobicity of the samples).
The results show that the amount of fluorine is directly correlated with the amount of oxygen : more high is the oxygen level on the sample, more important is the fluorine content till 0.7 ML, essentially in a O-Si-F bonding state. For more agressive etching leaving less than one monolayer of oxygen, the Si-F bond becomes predominant.

The ratio of the SiF to OSiF concentrations is a significant signature of the desoxidation state of the surface. Hydrophobicity of the wafer appears in the range of 25 % Si-F bonds. With very agressive etching processes, 66 % Si-F bonds and 33 % O-Si-F bonds are reached and the total amount of fluorine drops below 0.3 ML. For comparison, only Si-F bonds are oberved after a wet etching in a dilute HF bath without a rinse with a very low fluorine concentration.
The balance between Si-F and O-Si-F remains stable and seems to be representative of the surface states provided by the etching process.

1) - T.E MADEY and J.T YATES Jr. Chem. Phys. letters, Vol 19, n° 4, 487 (1973).

2) - A.F CARLEY and M.W ROBERTS Proc. Roy. soc A 363, 403 (1978)