HIGH RESOLUTION ICP-MS STUDY ON THE EFFECTS OF AMBIENT CONDITIONS ON NATIVE OXIDE GROWTH KINETICS FOR A SILICON <100> SURFACE

By: Fuhe Li, Marjorie K. Balazs, and Scott Anderson,
Balazs™ Analytical Services, Air Liquide America Corporation,
46409 Landing Parkway, Fremont, CA 94538

Winter Conference on Plasma Spectrochemistry, 2002

The presence of native oxide on a Si surface has been recognized as an impediment to the formation of the high-quality ultra-thin gate, atomic layer epitaxy, and small metal contacts on the surface [1]. Suppressing the native oxide growth during the surface cleaning and precisely controlling the interface prior to the advanced ultra-large scale integration processes have become crucial. This recognition has led to the considerable efforts of studying the growth mechanism of the native oxide on wafer surfaces and developing new analytical techniques that are capable of monitoring the ultra-thin native oxide on a Si surface, at or below a monolayer level.

The objectives of this paper are to extend our previous studies [2-3] of native oxide growth kinetics on a HF-cleaned Si <100> surface and to improve the analytical technique we reported previously for the oxide thickness measurements. We used a rapid acid-etching method to representatively extract the Si in oxide form from the wafer surfaces without removing elemental Si. The resultant solutions were directly analyzed by a double-focusing magnetic-sector based ICP-MS (HR-ICP-MS). The SiO_2 equivalent thicknesses in Å were then calculated based on the Si concentration, wafer surface area, and the density of SiO_2. During the course of the development, we have compared the HR-ICP-MS to the conventional quadrupole ICP-MS for the low-level Si determination. It was found that the HR-ICP-MS was more reliable than the conventional ICP-MS (the dynamic reaction cell and collision cell based ICP-MS were not investigated). This is due mainly to its ability to spatially resolve the $^{28}Si^+$ signal from the two commonly present polyatomic interferences, namely $^{12}C^{16}O^+$ and $^{14}N^{14}N^+$ (See Figure 1). The base-line removal of the interfering signals has lowered the Si background equivalent concentration (BEC), and more importantly improved the certainty of the analysis, especially when the amounts of dissolved molecular CO_2, N_2, HNO_3 and organic species (or TOC) present in the calibration standards and samples are inconsistent or unknown.

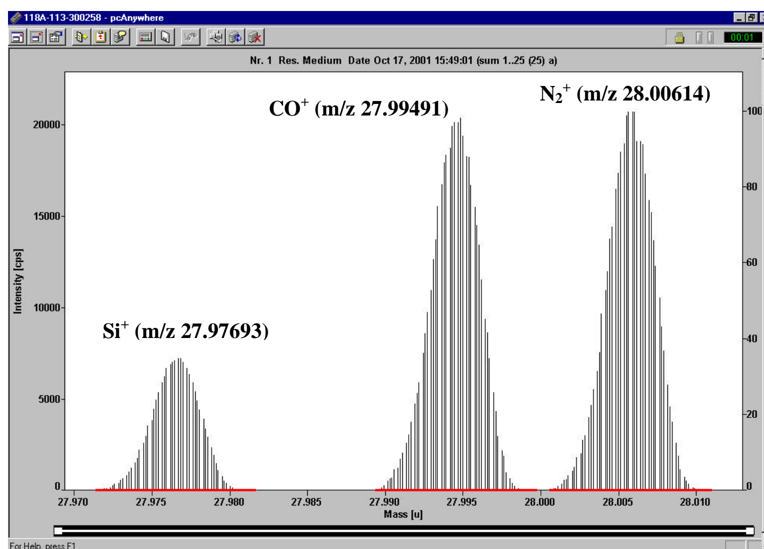

Figure 1. Background Spectrum acquired at medium resolution with 4000 resolving power.

The conversion of extractable Si concentration to oxide thickness was found to be difficult due to the lack of the enough information on the structure and density of the native oxide formed. The literature [4-5] has indicated that thin native oxide (10-100Å) formed on the surface is essentially a heterogeneous mixture of "SiO" and "SiO_2". At the interface of Si-SiO_2 structure, oxides thinner than 20 Å are not even fully stoichiometric, and there is a transition region in Si-SiO_2 structure (See Figure 2). The XPS studies of the 2p electron spectral line of Si atoms showed that the oxide has the form SiOx, with x increasing from 0 to 2 as the distance from the Si surface increases to greater than at least 10 Å. One way of estimating the thickness of the native oxide and being able to make direct comparison with others is to use SiO_2 equivalent thickness by assuming the oxides formed on a Si surface be complete SiO_2 and using its density for the thickness calculation. It should be kept in mind that the density of the native oxide with a thickness less than a monolayer might not be 2.2 gm/cm^3. Furthermore, at the interface, the thin native oxide may have large quantities of =Si=H_2 and ≡Si-H bonds [1] and may have an average form of SiOx with x between 0 and 1, e.g. Si_2O, without considering the hydration.

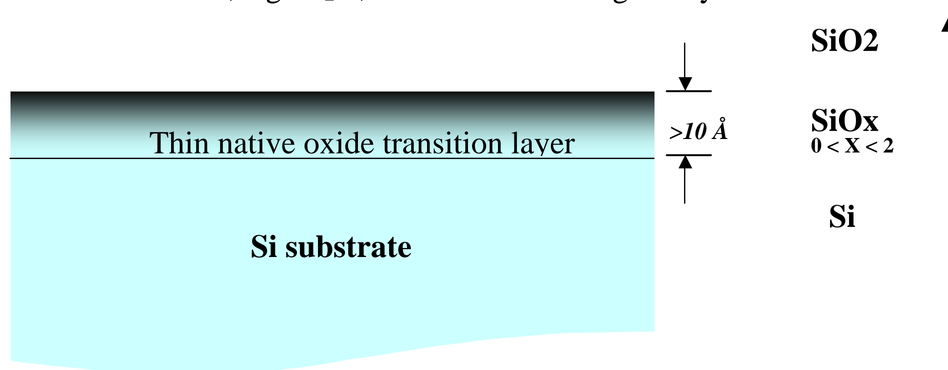

Figure 2. Cross-sectional schematic diagram of Si-SiO_2 interface.

Using the technique described above, we have studied the effects of ambient and dissolved O_2 concentration in UPW on native oxide growth on a Si <100> surface. The studies were focused on the

initial stage of the surface oxidation immediately after the HF-cleaning. The Si surfaces were exposed at a fixed duration to the UPW with different dissolved O_2 levels, open air, and dry N_2 respectively. The SiO_2 equivalent thicknesses of the ultra-thin native oxides formed on those surfaces were measured and compared. The results indicate that the ambient and the dissolved O_2 concentration in UPW dramatically affect the kinetics of the native oxide growth. Decreasing the dissolved O_2 level in UPW and protecting the ultra-cleaning with an inert and dry ambient may reduce or eventually prevent the native oxide from growing. Our data also indicates that by coupling the rapid acid-etching process with HR-ICP-MS, one can measure the thickness of the native oxides on a Si surface within a monolayer range. The resolution of this process has been proven to be <0.1Å, which ensures confidence in the accuracy of this method, given the approximate monolayer thickness of 4Å. This method can be utilized to monitor the native oxide growth and to help optimize the ultra-cleaning conditions. As an independent method, it may also be used for comparison with other techniques, such as ellipsometry, in which the refractive index used is no longer a constant for the ultra-thin oxides being measured.

[1] M. Morita, *Native Oxide Films and Chemical Oxide Films*, Ultraclean Surface Processing of Silicon Wafers, T. Hattori Ed., Springer, New York, 1998.

[2] F.Li, M.K. Balazs, and B.E. Deal, *Proc. of 18th SPWCC,* p125-141, Santa Clara, CA, March 1999.

[3] F.Li, M.K. Balazs, and B.E. Deal, *Solid State Technol*., 2000, **43**, 87.

[4] Y.J. Chabal, G.S. Higashi, K. Raghavachari, and V.A. Burrow, *J. Vac. Sci. Technol.* 1989, **7**, 2104.

[5] M. Morita, T. Ohmi, E. Hasegawa, M. Kawakami, and K. Suma, *Appl. Phys. Lett*., 1989, **55**, 562.