The effects of repeated chemical etching on the Si(111) surface : Shiraki oxidation

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The importance of chemical etching of Si surface has been emphasized due to its convenience as well as practicality for the preparation of clean and smooth substrate prior to processing. Usually the Si wafer is Ar^+ - sputtered and annealed in order to prepare the atomically chean surface under ultrahigh vacuum (UHV). Due to the locality and damage of the ion beam it is avoided in the industry.
Besides the limit of the sputtering, the annealing higher than 110°C is known to reduce the undesirable defects on the surface which shortens the life-time of the clean surface to the residual contaninants. Ishizaka and Shiraki had reported the series of chemical etching of Si(111) surfaces (such as degreasing, HNO_3 oxidation and etching, NH_4OH oxidation and etching, and Hcℓ treatment which forms very-thin oxide on the smooth surface.[1] The advantages of this passivating oxide are the preparation of carbon-free surface, inertness to the air during the transport, low-temperature (~800°C) annealing for decapping of thin oxide and the smooth surface beneath the oxide layer. In this paper we have monitored the characteristics of the Shiraki oxide using X-ray photoelectron spectroscopy (XPS), Low energy electron diffraction (LEED) and ultra-violet photoelectron spectroscopy (UPS). Since the pains-taking procedure of the chemical etching is not practical in the process, we compared the samples preserved in the deionized water, the air and the vacuum. The intensity ratio of Si 2p versus O_{1s} indicate the oxygen contents of the overlayer and the chemical shift of Si 2p indicates the oxygen coordination of SiO_x ($0.5 < x < 2$). The experimental results for differently prepared surfaces are summarized in table 1:

Preparation methods	O_{1s}/Si 2p Int. ratio	Chemical shift of SiO_2(eV)	SiO_2/Si in Si 2p	C_{1s}/Si 2p Int. ratio
Shiraki etched & UHV	1.29	4.5	0.093	0
Shiraki etched & in D-I H_2O	1.35	4.3	0.12	0
Shiraki etched & in air	1.16	4.4	0.10	0.4
Degreased native oxide	3.4	3.8	0.29	1.5
HF-etched Si(111)-M	0.16	non-detectable	non-detectable	0.6

In order the prepare the clean surface, oxygen and carbon should be removed. Since the substrates in the D-I. water or the vacuum do not have any chances to be contaminated by hydrocarbons, these substrates are quite good against SiC formation after annealing process. On the other hand the Si-H and Si-OH might brittle the surface structure in the substrate preserved in D-I water, as the high resolution electron energy loss spectroscopy reported previously.[2] Even if the passivated surface by the thin-shiraki oxide are relatively inert to the residual contaminats bote oxygen and carbon increased due to air-contaminants if it is exposed to air for a long time. We also found that HF etching efficiently removed the native oxide and passivated the surface to the molecules with oxygen, but the carbon could not be removed without Ar^+ - sputtering.

Another interesting results are observed in the LEED. Shiraki-oxide layer is so thin that 1×1 LEED pattern of the substrate had been detected without severe charging effect if we usee the primary energy of electron higher than 100eV. After the oxide layer is decapped at 900°C, the bright 7×7 pattern had been kept longer than 2 days under 1×10^{-10}mb. This indicates that the "clean" surface is not simply chemically-clean instead the surface should not have defect sites where the contaminants preferentially adhere.

As a conclusion, we have confirmed that the repeated chemical etching and oxidation reduces the subsurface defect sites and the final thin-oxidation passivate the surface to the residual gas contaminants. Therefore it is recommended to preserve in the vacuum condition (even if it is not high vacuum) in order to use the substrate like the freshly cleaned surface. Instead of high-temperature annealing for decapping of the thicker oxide than the shinaki-oxide, it is desirable to sputter "Lightly" prior to the annealing at the low temperature.

1. A. Ishizaka and Y.Shiraki, J. Electrochem. Soc., 133, 666 (1986).
2. J.M.Seo, "Dissertation ; Electron Scattering studies of Surface Phonon-Plasmon Modes of Semiconductors", Chap.6, U.M.I, Ann Arbor, Michigan (1990).