Investigations on Hydrophilic and Hydrophobic Silicon (100) Wafer Surfaces by X-Ray Photoelectron and High-Resolution Electron Energy Loss-Spectroscopy

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Abstract. The paper reports on surface spectroscopy measurements of silicon single-crystal wafers which have been treated in order to obtain hydrophilic and hydrophobic surfaces, respectively. The wafers are characterized in terms of the oxidation behaviour in air ("native oxides"), their surface chemical composition and the chemical bonds involved. It is shown that the oxide on hydrophilic wafers mainly grows in the cleaning agent and consists of hydrated SiO₂ through all stages of the growth. On a hydrophobic surface, however, the oxidation begins with the formation of a lower oxidation state which turns into SiO₂ on storage in air. The thickness of the oxides on both surface types reaches 1.4–1.5 nm. Both the chemical shift in photoelectron spectroscopy and the frequency of the asymmetric Si-O-Si vibration in electron energy loss spectroscopy support the assumption of a reduced bonding angle of the oxygen bridge.

Hydrophilicity is caused by singular and associated OH groups on the surface. Singular groups could be detected up to 700 K. There are hints that OH groups stabilize the oxide during heating. The hydrophobic state is mainly characterized by Si-H and Si-CHₓ groups on the surface, whereas Si-F exists only in minor quantities. Si-H groups were stable up to approximately 900 K in UHV. Si-CHₓ dehydrogenizes at temperatures between 500 and 700 K leaving SiC on the surface.

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Until recently the main goal of the electronic industry in wafer cleaning was to achieve a surface free of metal contamination. The test for a "good cleaning procedure" therefore mainly consisted in measuring the decline after immersion into the cleaning agent of a contamination (gold, copper, e.g.) intentionally fixed on a wafer [1]. This point being still of considerable interest, it is now generally accepted that with regard to high product yield and reliability of the production process the whole state of the surface has to be considered including contaminants like O, C, F, and H as well.

Especially the so called "native oxide" has gained attention, as it represents the stable state of the silicon surface after any cleaning procedure. A variety of cleaning methods for silicon wafers has been developed [2, 3]. These split into two categories whether they generate a hydrophilic or hydrophobic surface.

Among the "hydrophilic methods" the so called RCA cleaning [1] is the most widely accepted. It basically consists of an aqueous solution of ammonia and hydrogenperoxide. A hydrophobic surface is mainly achieved by the "HF" (hydrofluoric acid) dip with consecutive water rinsing.

Papers have been published mainly on the hydrophobic surface [4, 6–9]. It is reported that there are remarkable differences in the oxidation rate in high-temperature oxidation [4, 5]. Using high resolution ESCA Grunthaner et al. showed that the interface...
Si/thermal SiO₂ was spectroscopically different after different surface preparations [4]. The possible impact of surface chemistry on device performance was treated in a paper by Matlock [10] and especially for the case of hydrogen by Stein [11].

Because of the wet chemistry involved in the cleaning processes we have assumed H to play a significant role in Si surface chemistry. Hence we used a combination of methods to fully assess all aspects of these surfaces: ESCA (Electron Spectroscopy for Chemical Analysis) and HREELS (High Resolution Electron Energy Loss Spectroscopy).

1. Experimental

Samples were silicon wafers, boron doped in the range of 3–6 Ω·cm with (100) oriented surface, one side polished by a standard procedure [35], the other side etched. The hydrophobic treatment consisted of a short (1 min) hydrofluoric acid dip (5% aqueous HF) with a consecutive deionized water rinse. If the samples were not stored afterwards, they were inserted wet into the vacuum lock. The hydrophilic treatment was based on the work of Kern and Puotinen [1] with hydrogen peroxide as oxidizing agent. The wafers were stored in air in a usual wafer storage box. Reproducibility of the measurements was satisfactory and allowed the comparison of the ESCA and HREELS measurements, which were carried out at different places.

ESCA measurements were performed in a VG Escalab II spectrometer with a pressure in the 10⁻⁶ to 10⁻⁷ Pa range. Incident radiation was Mg Kα. The total experimental linewidth of the Si 2p line was 1.4 eV. If values of surface concentrations are given, Wagner's sensitivity factors [12] were used for computations.

The HREELS measurements were performed in a UHV system with a tandem electron spectrometer, capable of a resolution of about 40 cm⁻¹. Electron energy was 12 eV with an angle of the incident beam of 60° relative to the normal. Only specular reflected electrons were measured. Samples could be heated to approximately 700 K by radiation and to higher temperatures by electron bombardment from the backside. The samples were introduced via an air lock and the pressure during the measurements was in the 10⁻⁷ to 10⁻⁸ Pa region. If relative intensities are quoted they always refer to the noloss peak. In the following the term hydrophilic is abbreviated with “HL” and hydrophobic with “HB”.

2. ESCA Results

2.1. Oxides

Figure 1 shows changes in the Si2p spectra from freshly prepared surfaces to wafers, which had been stored in air at room temperature for different times up to one year. The thicknesses given are determined from the area ratio Si (oxidized)/Si (elemental) [13]. Values for the mean free path of photoelectrons in the oxide resp. Si were taken from [14]. These values (λ₆ = 2.3 nm; λ₆₀ = 2.5 nm) yielded the proper limiting oxide thickness (1.4 nm) for HF etched samples as confirmed with neutron activation analysis in [9].

The magnitude of the chemical shift (i.e., the difference in binding energy between Si elemental and Si