

ADSORPTION OF OXYGEN ON HF-ETCHED Si(111) SURFACES: XPS STUDY

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X-ray photoelectron spectroscopy studies of the Si(111) surfaces, after dilute HF etching and methanol rinse, are reported. These included a detailed analysis of the main core-levels (Si 2*p*, O 1*s*) and the valence band spectra. The observed asymmetry of the O 1*s* lines was attributed to two contributing subpeaks: the main (1) and the minor one (2), shifted ≈ 1.5 eV to higher binding energies. Their relative intensity was found to depend on the air exposure time and on the take-off angle. The peaks were assigned to two different positions of surface oxygen: (1) O chemisorbed with methoxy group, (2) bridging O atom. The valence band X-ray photoelectron spectroscopy spectra reveal the influence of surface states induced by the "chemisorbed O"-Si bond.

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1. Introduction

A silicon crystal held in air has a surface oxide layer of the so-called native oxide, which must be usually removed prior to inserting the sample into processing equipment or an experimental setup chamber. Such deoxidation occurs in a final stage of wet chemical treatment by dipping Si crystal in dilute HF, followed by adequate rinse. X-ray photoelectron spectroscopy (XPS) has been commonly used for investigating the microscopic structure of the HF-etched silicon surface, including single crystalline [1-5] and porous Si (e.g. [6]).

In the present paper, XPS measurements (including angle-resolved (AR) mode) of the HF-etched and air-exposed Si(111) surfaces are reported in an effort to understand better the binding structure of oxygen on silicon surface at the early oxidation stage.

2. Experiment

The samples used in the experiment, cut from the *n*-type float zone (FZ) Si single crystal (grown at the Institute of Electronic Materials Technology, Warsaw), had rectangular parallelepiped shape of $20 \times 10 \times 0.5$ mm³. Their front (111) surfaces were prepared by mechanical and chemical fine (device grade) polishing.

The room temperature XPS measurements were performed in a Vacuum Generators Escalab 210 spectrometer with a Mg K_{α} (1253.6 eV) irradiation source. In the standard configuration a detector axis was perpendicular to the sample surface (take-off angle, $\theta = 90^{\circ}$). Enhanced surface sensitivity was reached for $\theta = 20^{\circ}$. During the experiment the pressure in the spectrometer chamber was approximately 3×10^{-10} Tr.

Before each XPS measurement, the samples were subjected to the final wet chemical etching in aqueous HF (10%) solution, followed by the methanol bath. Typically, an air exposure of the treated specimens, prior to insertion into the spectrometer chamber, lasted about 4 min.

3. Results and discussion

The results of the experiment are listed in Table. This includes a detailed analysis of the main core-level (i.e. Si 2*p* and O 1*s*) spectra recorded for a typical sample after standard (4 min) air exposure (experiment *A*) and its twin sample (*B*), cut from the adjacent part of the same Si wafer. In the latter case (experiment *B*) the sample was subjected to longer (15 min) air exposure than the standard one. *B'* refers to the XPS spectra of the *B* sample, detected for $\theta = 20^{\circ}$.

TABLE
Summary of the core-level XPS analysis with simulation of the Si 2*p* and O 1*s* photoelectron lines and relative atomic ratio, [O]/[Si]. Γ denotes full width at half maximum.

Experiment	Si(2 <i>p</i>)			O(1 <i>s</i>)			Atomic ratio [O]/[Si]
	E_B [eV]	Γ [eV]	%	E_B [eV]	Γ [eV]	%	
<i>A</i>	99.3	0.84	66.0	531.9	1.92	85.0	0.105
	99.9	0.84	34.0	533.4	2.27	15.0	
<i>B</i>	99.0	0.94	66.0	532.1	1.93	71.0	0.830
	99.6	0.93	34.0	533.7	2.51	29.0	
<i>B'</i> ($\theta = 20^{\circ}$)	99.0	0.92	65.0	532.2	2.08	87.0	0.465
	99.6	0.91	35.0	533.8	2.03	13.0	

It was generally found in the standard case (*A*) that the Si 2*p* core-level spectra do not exhibit (see [5]) any additional features indicative of a chemical shift toward higher binding energies (E_B), that is characteristic of Si surface covered (even partially) with suboxides and/or SiO₂ (e.g. [3, 7, 8]) or with SiF_x [9]. Figure 1a illustrates the effect of longer air exposure (case *B*, *B'*) on the Si 2*p* spectrum recorded by the AR XPS. It is evident that, despite prolonged exposure, one observes here only residual contribution of different suboxides in the range 100–104 eV.

The numerical analysis of the Si 2*p* and O 1*s* spectra, performed by fitting them with Gaussian-Lorentzian component peaks (Table), provided more information about the structure of the partially oxidized Si surfaces studied. It can be

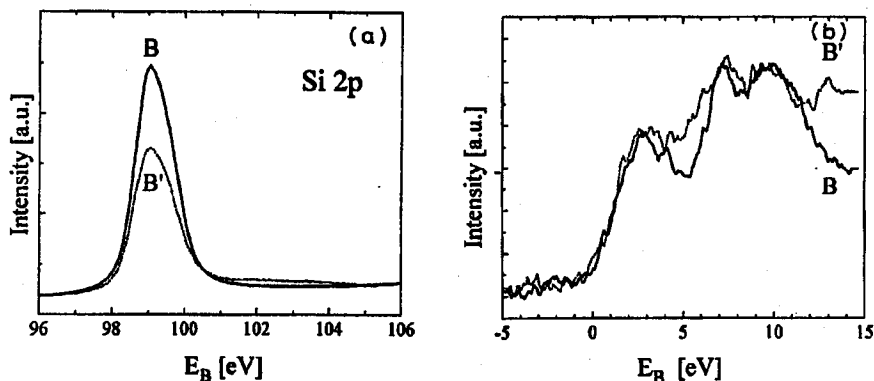


Fig. 1. Si 2p XPS spectra (a) and the valence band XPS spectra (b) recorded at the take-off angle 90° (solid line) and 20° (dashed line) for the Si(111) surface, subjected to prolonged air exposure (case *B*, *B'* — respectively).

seen that the simulation of the recorded Si 2p peaks (case *A* and *B*) revealed a typical doublet split by 0.6 eV, with the intensity ratio $I(p_{3/2})/I(p_{1/2}) \approx 2$ (e.g. [8]). The O 1s core-level spectra recorded here exhibited slight asymmetry indicative of the initial oxidation stage of the Si surface (see e.g. [10]). Their simulations enabled us to distinguish (similarly as in [11]) two component peaks: the main peak at $E_{B1} = 532$ eV, and a minor one (at E_{B2}) shifted by about 1.5 eV to higher binding energies.

Since the magnitude of $E_B(\text{O } 1s)$ for the oxygen adsorbed on Si surface depends on the oxide thickness [7, 12], the observed binding energy of the main O 1s component indicates that in our experiments (*A*, *B*) the effective thickness of suboxides remains below 5 Å. However, a weak shift (0.2 eV) of E_{B1} and E_{B2} to higher binding energies, resulting from increased air exposure (case *B*), is noticeable from Table. This correlates with an increased [O]/[Si] atomic ratio (Table). One should pay here special attention to the contribution of the E_{B2} component to the total O 1s line intensity (I_t). After prolonged air exposure (*B*) the ratio $I(E_{B2})/I_t$ became nearly double. On the other hand, the relative contribution of peak 2, measured in an increased surface sensitivity mode (*B'*), was significantly reduced.

The observed relative changes of both component peaks to $I_t(\text{O } 1s)$ could be explained by their assignment to two different nonequivalent binding positions of oxygen atom on the Si surface. The second peak (E_{B2}) can be identified with bridging O atoms in the top Si layers whereas the main one (E_{B1}) can be related to the chemisorbed O atoms. Since the etching process applied here was followed by methanol bath it seems likely that oxygen remains chemisorbed in a methoxy group thus leading to formation of a stable surface species SiOCH_3 [13, 14]. Our present assignment seems to contradict the one previously introduced in paper [11] — however, it should be emphasized here that its authors have not applied the AR-mode in their photoemission experiment.

Additionally, Fig. 1b presents the valence band (VB) XPS spectra recorded at the take-off angle 90° and 20° for the Si surface, subjected to prolonged air exposure (case *B*, *B'* — respectively). The VB spectrum *B* consists of three peaks, located near 3, 7.5 and 10 eV, which remain characteristic of Si(111) [6]. Its comparison with analogous spectrum measured for enhanced surface sensitivity (*B'*) clearly reveals the surface-related features located near 5 eV and 13 eV. They can be attributed to the contribution of surface states induced by the “chemisorbed oxygen”–Si bond, denoted in literature by O_b and O_σ [15], respectively, thus remaining in agreement with the model considered.

4. Conclusions

The above analysis of the XPS data for the HF-etched Si(111) surfaces indicates (within our air-exposure time) that oxygen is adsorbed on Si surface with only residual coverage by Si oxides. It also enabled us to explain the asymmetry of the O 1s XPS peak by a model of two contributing subpeaks and to achieve a suitable assignment to different bond configurations of oxygen with host atoms on Si surface.

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