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XPS Study of α-Quartz Surface

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XPS spectra of quartz annealed in UHV at 500°C or sputtered with Ar^+ ions show the appearance of satellites of Si 2*s* peak at 2.0 eV, the surface ratio of O : Si attaining the value of 1.55. Formation of Si^{3+} ions with nonbinding electrons is postulated.

Introduction

The structure of the clean quartz surface has been a subject of interest for many years, as it may be expected that on such a surface, obtained either by cleaning or by cleavage of a crystal, the regular tetrahedral arrangement, characteristic for the ideal SiO_2 lattice (*1–4*), must be disturbed. The perturbation involves also the state of valence electrons in surface atoms. A considerable number of unpaired electrons was detected by ESR in quartz milled under UHV (*5*) or dehydrated by high-energy photons (*6–8*). The ESR signal is suppressed on exposure of the clean quartz surface to air due to adsorption of water and gases. The oxidation of quartz powder in flame has also been reported (*9*).

These observations were explained by assuming the existence of free radicals on the surface, localized either on silicon or oxygen atoms. They could be electrons (*4*) or electron pairs (*3*). Also rehybridization of silicon orbitals and formation of $Si{=}O$ (*3*) as well as decrease of the silicon valency to +3 (*10*) or even to +2 have been proposed. Hübner (*11*) has recently postulated a random-bonding model for SiO_x compounds assuming the statistical distribution of five types of tetrahedra containing different numbers (from 1 to 5) of silicon atoms. The problem of the lower valency of silicon is not restricted to the quartz surface. It usually is assumed that in glasses the 10- to 30-Å clusters are present having the structure of high-temperature crystobalite. Boundaries of such clusters must be disordered and populated with broken Si–O bonds, resulting in the presence of silicon atoms of lower valency (*12*). It seemed thus of interest to study the structure of the quartz surface by photoelectron spectroscopy in order to discriminate between the different models.

Experimental Results

The measurements were performed with an ESCA-3 Vacuum Generators spectrometer. Samples of Brazilian quartz in the form of discs (A) 8 mm in diameter and 2 mm thick, as well as rectangular plates (B) $10 \times 8 \times 0.4$ mm in size were etched in $H_2F_2 + H_2SO_4$ solution (A) or $H_2F_2 + HCl$ solution (B) and then were carefully washed with H_2O and C_2H_5OH. A very small amount of gold was evaporated in the spectrometer chamber

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onto the surface of sample B for the calibration of spectra. The spectra were recorded just after a vacuum of 10^{-8} Torr was attained, after advanced annealing of sample A for 2.5 hr at 600°C or of sample B for 10 hr at 100°C, and after Ar^+ ion bombardment (15 min, 500 eV) of sample A and annealing (10 hr, 500°C) of sample B.

Recorded spectra of sample A were calibrated against the C 1*s* line (285.0 eV) and those of sample B against the Au 4*f* (84.0 eV) line. Sample A, unlike sample B, showed a distinct charging effect (+1.7 eV). Moreover, the comparison of spectra of samples A and B indicated that the C 1*s* line under thermal treatment was floating (287.3, 286.9, and 286.0 eV) while charging amounted to 1.7, 2.0, and 1.5 eV, respectively. This result has confirmed our earlier observations showing that the C 1*s* line is unsuitable as standard, if the surface is treated with active redox agents. Charging of sample B was small (about 0.2 eV) and binding energies (BE) determined for this sample were taken for further discussion after correction against the Au 4*f* peak position (Table I).

The O 1*s* peak from the surface "as received" contained a shoulder at the high-binding-energy side, disappearing after annealing, probably due to oxygen from hydroxide groups which always are present on the surface. The content of water in the bulk, as determined by IR spectroscopy, amounted to less than 10 ppm. It seems thus that the influence of water or OH groups may be neglected.

TABLE I

BINDING ENERGIES OF ELECTRONS AND SURFACE COMPOSITION OF QUARTZ SURFACE

Surface treatment	BE of electrons (eV) Si 2_p	Si 2*s*	O 1*s*	I(O)/I(Si) Ratio
As received	103.9	155.0	533.4	2.0
Vacuum, 10 hr, 100°C	103.6	154.8	533.1	1.83
Vacuum, 10 hr, 500°C	103.7	154.8	533.3	1.55

The shape of the Si 2*p* line in the course of the whole experiment did not change having FWHM = 2.4 eV.

The Si 2*s* band from the surface "as received" was symmetrical. However, after Ar^+ bombardment or after prolonged annealing at 500°C on the high-binding-energy side of the peak a distinct shoulder (Fig. 1) grew. Deconvolution of the curve (Fig. 2) showed that the new peak was shifted from the parent peak by 2.0–2.5 eV. In the spectrum of the annealed sample also a second new peak on the higher-binding-energy side was visible (Fig. 1) at a distance of about 9 eV.

The last column of the table contains the ratio of the number of oxygen atoms to silicon atoms, calculated under the assumption

FIG. 1. The Si 2*s* bands from the surface of Brazilian quartz. Curves 1 and 3 are from the samples "as received." Curve 2, after annealing under vacuum for 10 hr at 500°C. Curve 4, after Ar^+ bombardment (500 eV, 15 min).

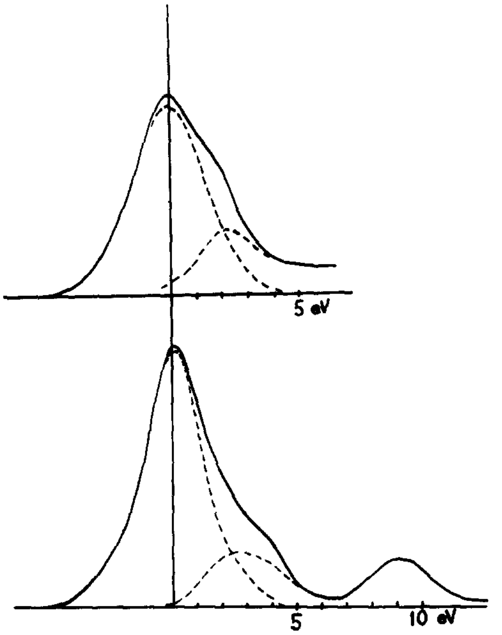

FIG. 2. The deconvolution of Si 2*s* bands from Fig. 1 (curves 2 and 4).

that the number of surface atoms is proportional to a peak area and that the composition of the surface "as received" corresponds to the ratio Si : O = 1 : 2.

Discussion

The BE value of Si 2*p* electrons (E_B = 103.9 eV) determined in the present investigation is in agreemeent with that reported by Carriere *et al.* (*13*) for natural quartz. Heating of quartz at 100°C generates changes characterized by a decrease of charging, a small shift of the BE value, and a decrease of the number of surface oxygen atoms by about 8.5%. The BE shift, if not due to aggregation of gold (*14*), may reflect a change in the electronic structure. It does not seem to result from the Fermi level shift, taken as the origin of the BE scale, as the experimental data (*15*) indicate that the work function value of SiO_2 (5.0 eV) is close to that of Si (4.8 eV) and it may be thus assumed that it will not change upon reduction of SiO_2. The decrease of the number of oxygen atoms and of the BE value probably results from the dehydration of the surface and breaking of chemical bonds. The evolution of water entails the removal of terminal OH groups from surface tetrahedra and the appearance of paramagnetic electrons trapped on surface levels.

More energetic treatment, such as argon ion bombardment or prolonged annealing at 500°C under high vacuum, leads to more distinct changes in the spectra. The appearance of a nearer satellite peak (about 2 eV) may be due to the multiplet splitting (*16*) or energy losses of photoelectrons accompanying optical transition, probably from the trap levels (2–3 eV) to the conduction band (*17*). A second peak lying about 9 eV away from the parent peak may represent the losses due to transitions from nonbonding $5t_2$ orbitals to the conduction band. But, irrespective of the mechanism of the observed losses, their appearance requires the presence of quasi-free, nonbonding electrons and such conditions are only realized in the reduced surface layer. Results of the present work permit one to eliminate from the considerations the formation of SiO, as the chemical shift accompanying the change of valence from +4 to +2 is about 1 eV (*11, 18*). Reduction of silicon from +4 to +3 entails no chemical shift (*11*) or a small one not exceeding 0.3 eV, as assumed in the present work. Simultaneously the ratio of oxygen-to-silicon atoms attains the value of 1.55. Both arguments lead us to the conclusion that after reduction the quartz surface contains trivalent silicon atoms.

The present results have been obtained under high vacuum. After annealing under such conditions the whole layer (about 40 Å) controlled by measurements was reduced, i.e., the regular SiO_2 lattice was destroyed with simultaneous oxygen evolution and appearance of quasi-free electrons in the amount one per silicon atom.

The question may be raised as to whether these electrons are nonbonding and unpaired, decreasing silicon valency to +3, or whether they form Si–Si bonds, rendering the silicon valency more statistical in character (*11*). The satellite lines observed by us on the high-binding-energy side of the Si 2*s* lines resulting from the presence of unpaired electrons favor a classical valency model with Si^{3+}. This state is stable at the surface under vacuum or in other environments free of oxygen and water, e.g., at the surface of clusters inside the glass phase.

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