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(0001) quartz surface imperfections

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Abstract

Monocrystalline (0001) quartz surfaces may present two kinds of imperfections : point defects (surface oxygen vacancies) and tridimensional disorder (superficial amorphization). The point defects are studied thanks to Reflection Electron Energy Loss Spectroscopy experiments, which show that electronic transitions (5.1 and 7.2 eV) associated with surface oxygen vacancies appear in the gap of α-quartz under ion or electron bombardment and 900°C vacuum heating. The defects responsible for these structures are located in the first nm under the surface. X-ray Absorption Near Edge experiments (XANES) at the O K-edge show that the 900°C vacuum heating leads moreover to the destruction of the surface crystallinity (≈5 nm), as proved by the modification of the multiple scattering structures.

1 - Introduction

Silicon dioxide is one of the most widely studied materials, owing to its technological interest, which ranges from precision oscillators to optical fibers and dielectric materials. The surface properties of SiO_2 are often determinant in its applications, and studying α-quartz provides information that can furthermore be profitable for the different crystallographic forms of SiO_2. In previous papers, we have studied the reconstruction of the $(10\bar{1}0)$ [1] and (0001) [2] surfaces, and the electronic structure of their defects [3]. A complete understanding of the defects present on silica surfaces would be of great importance for a better understanding of electrical or piezoelectric properties.

2 - Experimental

2 - 1 - Samples

The samples were square slabs of high purity α-quartz (SICN) of 500 μm thickness, cut normal to the Z-axis, noted (0001) with the Miller indexes. After a careful mechanical polishing (up to optical-use specifications), each quartz plate was chemically etched in a 2% diluted HF solution for 5 minutes, and heated at 900°C in air, so as to present a reconstructed electron diffraction pattern

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[2], characteristic of a well-ordered surface. Some samples were then heated under vacuum (10^{-8} mbar) at 900°C during 1 hour; some others were ion bombarded (Ar+, 7 keV, 70 µA during 20 minutes). The surface chemical purity was probed by XPS (X-Ray Photoelectron Spectroscopy). XPS and LEED results are described in ref. [1]. The surface was free of carbonaceous or fluorine contamination, within the detection limit of XPS (about 1 % monolayer).

2 - 2 - Methods

REELS, as well as XPS and LEED experiments, were carried out in a MECA 2000 UHV system (work pressure 10^{-10}mbar). The analysis chamber is fitted with an electrostatic electron gun (Riber CER 610), the resolution of which is 0.7 eV for a primary energy of 150 eV. Reflection Electron Energy Loss Spectroscopy (REELS) has the advantage of extreme surface sensibility, for properly chosen primary energies Ep, because of the low mean free path of electrons (about 1 nm at 350 eV).

X-ray absorption spectra were carried out on the SA72 beam line at the super-ACO synchrotron facilities (LURE, Orsay). This lines provides photons in the 150-1500 eV range, allowing oxygen K-edge absorption studies et about 530 eV. The spectra were taken in the total yield detection mode. The energy resolution at 500 eV is about 0.5 eV.

3 - Results and discussion

3 - 1 - Oxygen vacancies

The structures appearing in the electron loss spectrum of a solid are related to electronic transitions from occupied to empty states. They are more precisely associated to the maxima of the dielectric loss function $\mathrm{Im}\left\{-\frac{1}{\varepsilon}\right\}$ [4]. When point defects are present, they induced localized electronic energy levels within the forbidden band. They may consequently involve electronic transitions of energy lower than the forbidden gap width.

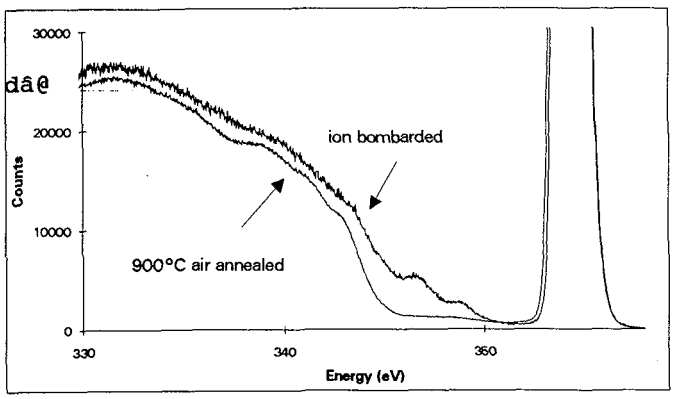

figure 1 : REELS spectrum of two α-quartz surfaces at Ep=350 eV : the upper curve corresponds to the ion bombarded sample (Ar+, 7 keV, 70 µA during 20 mn) and the lower curve corresponds to the 900°C air annealed surface. The width of the surface band gap is equal to 7.6 eV for the upper curve and to 9.1 eV for the lower one. The elastic peaks are normalized to the same intensity.

The figure 1 represents two REELS spectra taken at a primary energy of about 350 eV, corresponding to an electron mean free path of 1 nm. The lower curve is related to the air annealed sample and the upper curve to the ion bombarded sample. The width of the surface band gap, as measured by the first loss (excepted the defect losses), is respectively equal to 9.1 and 7.6 eV. The vacuum air treatment, as well as the ion bombardment induce the presence of two states within the band gap, as shown on figure 1, which are a spectroscopic sign of point defect present on the surface.

These defect losses appear also under the electron beam used to carry out REELS experiments. Furthermore, their presence has no connection with the existence of a well defined LEED pattern. Indeed, we have checked that the crystallographic orientation of the sample, (0001) or $(10\bar{1}0)$ does not lead to noticeable differences in the energy of the levels. It is important to point out that these two levels are strongly correlated, since their intensity ratio was constant during the whole set of experiments. The energy of the higher energy defect level measured on different samples, for different primary energies varying between 180 and 1000 eV is around 7.3 ± 0.2 eV. The same experiments lead to 5.25 ± 0.15 eV for the lower one. The spreading of the measured energies is certainly due for a large part to the well known charging problems that we must face when working on insulating materials [5]. It may also be attributed to the instability of the primary electron beam. We have checked that, for Ep=1350 eV, where the mean free path of the electrons is equal to 3 nm, the structures are no more visible. The defects are consequently located in the first nm of the α-quartz sample. The loss spectrum is further discussed in ref. [3].

The question is to determine the defect(s) that is involving the 5.1 and 7.2 eV transitions. The intrinsic defects of SiO_2 (amorphous or crystalline) [6] may be divided in two families which are first the oxygen related defects and second, the silicon related defects. Among the latter is the bulk oxygen vacancy, which may be neutral V_O^* (also described as the weak ≡Si...Si≡ bond) or positively charged V_O^+, and thus corresponding to the E' center. The oxygen vacancy may also exist at the surface of SiO_2. In this case, it is made of a non bridging silicon atom [7].

The first conclusion of our experimental study is that both levels are correlated to the same defect since the ratio between their intensities remained constant during the whole REELS works. Our experiments also demonstrate that both levels are intrinsic of SiO_2, since they remain the same whatever the way they are created: by a phonon excitation (UHV heating), by an electronic excitation (interaction with the 350 eV electron beam) or by an atomic excitation (collision between the 7 keV Ar^+ ions and the nuclei of the surface and near-surface atoms). It is very well-established that ion-beam-induced alteration of the composition and the structure of oxides is most of the time leading to preferential loss of oxygen. The effect of Ar+ bombardment in the 1-10 keV energy range on SiO_2 is the surface depletion in oxygen [8,9,10]. The observed defects appear also under electron bombardment, even at energies of 350 eV. This observation is to be compared with the work of Baragiola et al. [11], who has observed ESD (electron stimulated desorption) of multiple charged ions from SiO_2. This work demonstrates that the best efficiency is obtained when the electrons have approximately 300 eV. These remarks lead to the unambiguous conclusion that these transitions are associated with oxygen vacancies. They are more precisely associated to the surface oxygen vacancy.

3 - 2 - Tridimensional disorder

The figure 2 gives the O K-edge spectra recorded for three samples : a reconstructed quartz sample (lower) [12], a 900°C vacuum annealed quartz sample and (mean) an amorphous silica sample (upper). The 900°C vacuum heated sample spectrum is close to the amorphous sample one.

Since the 900°C vacuum heated sample spectrum resembles to the amorphous sample one, we can consequently conclude that the vacuum heating induces the superficial amorphization of quartz. This hypothesis is also supported by the absence of LEED pattern on the vacuum annealed

samples. This amorphization may be due either to the effect of the vacuum heating, which is supposed to introduce some disorder in the periodicity of the lattice, or to the rather fast cooling of the sample. Whatever may be its origin, this observation is to be compared with the chemical particularity of SiO_2, which can exist in an amorphous state.

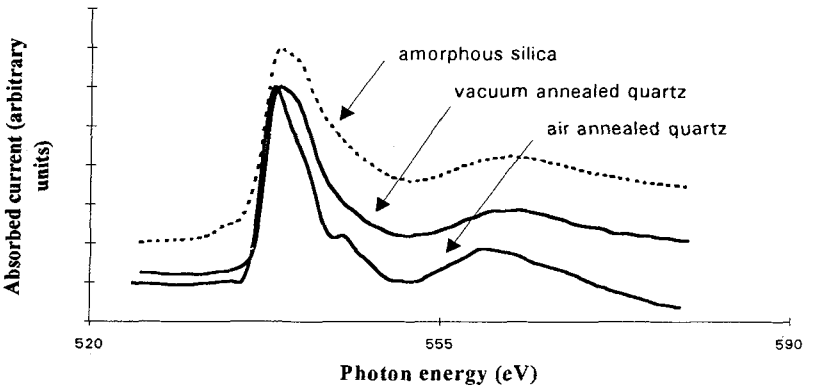

figure 2 : oxygen K-edge absorption spectra of reconstructed quartz (lower), 900°C vacuum annealed quartz (mean) and amorphous silica (upper).

4 - Conclusion

The surface of monocrystalline (0001) α-quartz sample may present two kinds of surface imperfections, point defects and tridimensional disorder. On one hand, oxygen vacancies appear in the last nanometer under the surface, after ion and electron bombardment, and UHV heating. These point defects are easily probed thanks to Reflection Electron Energy Loss Spectroscopy, which shows the presence of two transitions within the band gap of SiO_2 , at 5.1 and 7.2 eV. On the other hand, the comparison between oxygen K-edge absorption spectra of quartz and of amorphous silica permits to conclude that the surface of quartz becomes vitreous after a 900°C vacuum heating.

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