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Quantification of outermost OH group on silica glass surface by high-resolution elastic recoil detection analysis

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ABSTRACT

High-resolution elastic recoil detection analysis (HERDA) has been conducted to quantify outermost OH group on a silica glass surface. The results of HERDA showed that the surface number density of OH groups (silanol number) can be measured with a good reproducibility by heating the sample in vacuum to remove the surface adsorbates. The measured silanol number depends on the temperature and is in good agreement with the result reported for porous silicas. Furthermore, by investigating the relationship between the contact angle of water and the silanol number, it was confirmed that the contact angle increases with decreasing silanol number.

1. Introduction

Flat sheet glasses are widely used not only for buildings and automobiles but also for electronic devices such as substrates for display devices and solar cells. In these applications characterization and control of glass surfaces and interfaces are of prime importance. For example, depth profile analysis of glass surface has been carried out to investigate the relation between the diffusivities of mobile ions and the chemical durability of glass [1–6]. Recently, it was demonstrated that X-ray photoelectron spectroscopy (XPS) in combination with C_{60} ion sputtering enables an accurate depth profile analysis, and this method was successfully utilized for elucidating various phenomena, such as migration of modifier ions [7–11]. However, XPS cannot detect hydrogen although hydrogen often plays an important role. The depth profile of hydrogen in the surface region was sometimes measured using dynamic secondary-ion mass spectrometry (D-SIMS) [3, 4, 10, 12–14] and nuclear reaction analysis (NRA) [12, 13, 15–17]. D-SIMS has an excellent sensitivity but the quantification is problematic. On the other hand, NRA provides quantitative analysis but requires a rather large facility *i.e.* an ion accelerator facility. It was shown that when the glass surface reacts with water, the modified ions (alkali metal and alkaline-earth metal) are exchanged with protons or hydronium ions at the alkali silicate glass surface [10, 13, 15]. It is, however, noteworthy that the depth resolution of these techniques are not good enough to measure hydrogen in the outer most surface separately from that in the bulk.

The surface OH group (Si-OH) on glass surface has been extensively investigated by various surface analytical methods, for example, D-SIMS [10, 18], NRA [12, 13, 15–17], XPS [19, 20] and mass spectrometric thermal analysis [21, 22], because the surface OH group influences important properties such as hydrophilicity, adhesion, adsorption and chemical durability. The outermost OH group of various amorphous silica materials was reported by Zhuravlev [22]. In the study, the surface Si-OH content was estimated by mass spectrometry of the Si-OD state after the glass was maintained in a heavy water atmosphere to replace the surface Si-OH with Si-OD. The surface Si-OH content is reported as 4.6 nm^{-2} for the outermost surface of various amorphous silica materials, which agrees well with the value obtained with molecular dynamic simulations by Du et al. [23]. It was also demonstrated that the surface Si-OH content decreases with increasing temperature and almost disappears at 1100 °C. The sensitivity of this method, however, is not good enough to measure Si-OH on a flat silica surface. They can measure only porous silicas or small silica particles having a large specific surface area ($> 10\ m^2\ g^{-1}$). Recently, Suzuki et al. investigated the correlation between the surface OH group and the contact angle of water [24]. They reported that the contact angle of the flat silica glass increased from 5° to 33° with the heat treatment at 850 °C under an N_2 atmosphere, and then gradually decreased with elapsed time in the air and finally reached the similar value before the heat treatment. This suggests that the surface OH content was reduced by the heat treatment and recovered with time to the initial value in the air, which was qualitatively confirmed by D-SIMS measurements. However, the quantification of outermost OH groups has not been achieved yet since D-SIMS suffers from the surface transient effect. D'Souza et al.

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determined the surface OH content of silica rod surfaces by static ion mass spectroscopy in combination with Fourier-transform infrared (FTIR) and XPS [25]. Unfortunately, the detection depth of their method (1–2 nm) does not allow to measure the outermost OH separately from the bulk OH. In addition, precise quantification in SIMS techniques is difficult due to the variation in the secondary ion yield of an element contained in different matrices, *i.e.* the so-called matrix effect [26].

High-resolution elastic recoil detection analysis (HERDA) is a suitable technique for investigating hydrogen in the surface region [27–30]. HERDA has a much better depth resolution of 0.2 nm than other conventional techniques, and are able to quantify the amount of hydrogen in the outermost monolayer without the matrix effect [30]. Nevertheless, there has been no HERDA measurement of the OH group on a glass surface. The main objective of this paper is the development of a methodology for the quantification of outermost OH group (silanol number) on a glass surface. Using the developed method, the effect of thermal treatment on the silanol number is investigated and the result is compared with that of porous silicas. Furthermore, the relation between the silanol number and the contact angle of water is examined.

2. Experimental procedure

Commercial silica glasses were obtained from Asahi Glass Co., Ltd. The glass samples were cut into thin plates with a thickness of 0.7 mm, polished with an automatic polisher and treated with 0.1% HF for 1 min. For the preparation of "850 °C" sample, a silica glass after the HF treatment was heat-treated at 850 °C for 8 h in an electric furnace under an N_2 atmosphere the dew point of which was less than –20 °C.

The contact angle of water was measured with the θ/2 method by using a Drop Master DM-701 (Kyowa Interface Science Co., Ltd., Niiza, Japan). The measurement was carried out five times for each sample and the uncertainty was evaluated as the standard deviation (σ) of the five measurements. The contact angle was confirmed to remain constant during the measurement for several minutes after droplet deposition. Prior to each measurement, the sample surface was treated by UV/O_3 cleaning for 10 min with a UV Ozone processing unit (SEN LIGHT CORPORATION, Toyonaka, Japan). Since the organic contamination was removed with UV/O_3 cleaning [20], sample surfaces in the present study were free from organic contaminations.

The details of the HERDA measurement were described elsewhere [30]. After the UV/O_3 cleaning, a glass sample was mounted on a 5-axis goniometer in an ultra-high vacuum scattering chamber (base pressure 1×10^{-8} Pa). The goniometer had a heater to control the sample temperature up to 500 °C. The chamber was equipped with an electron flood gun to prevent possible charging during the HERDA measurement. Carbon ions were produced by a PIG (Penning ion gauge) type ion source and accelerated to 300 keV. The C^+ ion beam was collimated to $2 \times 2\,mm^2$ using two sets of 4-jaw slit systems. The typical beam current was 5 nA. The samples were irradiated with the C^+ ion beam at an incident angle of 68°. Hydrogen ions recoiled from the sample at 25° with respect to the incident direction were analyzed using a magnetic sector spectrometer and detected by a one-dimensional position sensitive detector. A thin Mylar foil of 0.5 μm thickness was mounted in front of the detector to reject carbon ions scattered from the sample [29]. This is crucial to reduce the possible background caused by the low energy carbon ions scattered from the sample. A Kapton® thin film (Dupont-TORAY Co., Ltd.) with a thickness of 8 μm was used as a calibration standard for the hydrogen quantification. The errors of the quantification consist of two parts, the statistical errors (random errors) and the systematic errors. The statistical errors were estimated as the square root of the detected H^+ counts. The main contribution to the systematic errors was the error in the calibration measurement and was estimated to be 5%.

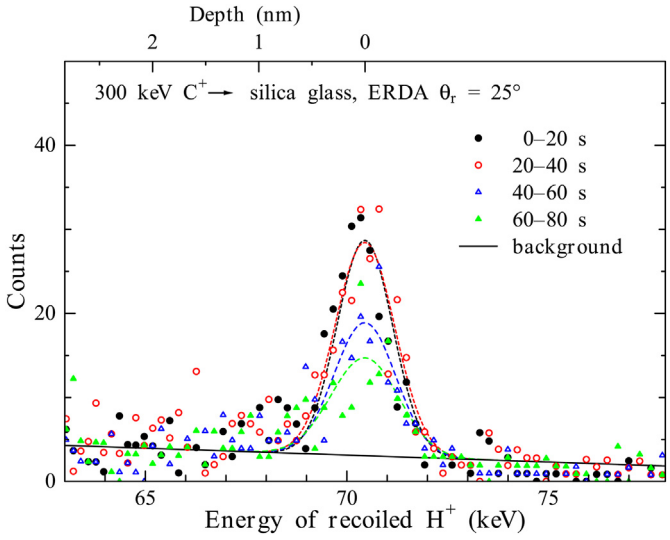

Fig. 1. Examples of HERDA spectra observed in a series of short measurements for a silica glass. The depth scale is also shown in the upper abscissa. The solid line shows the estimated background.

3. Results and discussion

Fig. 1 shows examples of energy spectra of recoiled H^+ observed in a series of short measurements for a silica glass. Using stopping powers of silica glass for C^+ and H^+ ions, the energy scale can be converted to the depth scale and shown in the upper abscissa. All spectra have a sharp peak at ~70.5 keV, which corresponds to the hydrogen in the outermost layer. The full widths at half maximum (FWHMs) of these peaks are about 0.6 nm, which are larger than the depth resolution (0.2 nm [30]) of our HERDA apparatus. This is partly because the amorphous silica surface is not atomically flat. The observed peak becomes smaller with C^+ ion irradiation, indicating that the hydrogen atoms are desorbed by the irradiation. It should be noted that there are some signals at energies higher than 72.5 keV where no H^+ signal is expected. These background signals are attributed to the detector noise and recoiled light elements other than hydrogen. These background signals were fitted by a straight line and the result is shown by a solid line. The correlation coefficient of the fitting was 0.82. By subtracting the background, the net hydrogen yield was derived and the number density of surface hydrogen was estimated from the derived yield. In this estimation, the Kapton film was used as a calibration standard. The measured hydrogen density was plotted as a function of the irradiation time t in Fig. 2. The yield decreases rapidly with t and becomes almost constant after about 200 s. The rapid decrease is attributed to the desorption of the OH groups due to the ion irradiation. The time-independent behavior at $t > 200$ s indicates that the adsorption of OH groups also occurs presumably due to the hydrolysis reaction of residual water vapors on the surface. The behavior of the surface hydrogen density $Y(t)$ can be described by the following equation

$$\frac{dY(t)}{dt} = -I\sigma Y(t) + \alpha, \tag{1}$$

where I is the ion flux, σ is the hydrogen desorption cross section and α is the adsorption rate of the OH group. The solution of Eq. (1) is given by

$$Y(t) = Cexp(-t/\tau) + \tau\alpha, \tag{2}$$

where $\tau = 1/I\sigma$ and C is a constant.

The measured result was fitted by Eq. (2) and the fitting result is shown by a dashed line in Fig. 2. The correlation coefficient of the