In situ Measurements of the Desorption of Water from a TiO₂ Surface under Dry Air by Collecting the Photoemission Yield with an Open Counter

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We investigated the desorption of water from a TiO₂ surface under a dry atmosphere by collecting the photoemission yield spectra with an open counter. For this purpose, a new attachment for the photoemission yield measurement was prepared. This apparatus is capable of detecting, in the open air, low-energy electrons excited by photons under dried atmospheres; the dew point is below –35°C. A significant change in the photoemission yield spectra due to exposure to a dry atmosphere was observed. To gain a better understanding of these results, observations of the change in the photoemission yield spectra caused by the thermal desorption of adsorbed water were also carried out. The results are consistent with those obtained by exposure to a dry atmosphere. Based on the relationship between the photoemission yield and the thickness of the water layer, the time dependence of the change in the thickness was explained by the second-order reaction rate equation.

Keywords Photoemission yield measurements, dry atmosphere, anatase, titanium oxide, adsorbed water, work function

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Introduction

Surface analysis techniques, such as X-ray photoelectron spectroscopy (XPS), Auger electron spectroscopy (AES) or time-of-flight secondary ion mass spectroscopy (TOF-SIMS), are widely used for the characterization of solid surfaces. Chemical reactions, such as oxidation, reduction, and catalytic action, proceed on the solid surfaces. However, most studies concerning solid surfaces have been performed in an ultrahigh vacuum, giving information on the static states of the surfaces. It is expected that electronic structure analysis on the surface of a solid can be performed in a practical atmosphere, at which the surface is operating or functioning. Such analysis can be done by using a photoemission yield spectrometer in air (PYSA), which employs the open counter1–4 as the detector. The open counter can detect and count a small number of low-energy photoelectrons, and can be operated in air under atmospheric pressure. Therefore, the observation of successive changes on a practical surface, such as Al exposed to air,1 has been successfully performed. We then applied PYSA to measurements under a controlled atmosphere.

In this work, we prepared a new type of PYSA equipped with a dry attachment, which can analyze a sample surface at the dried atmosphere. In order to confirm the performance of this newly designed PYSA, we measured titanium dioxide (TiO₂).

TiO₂ is one of the most attractive photocatalytic materials owing to its high oxidizing and reducing power,6 high chemical stability and abundance of titanium. The relationship between the surface electronic structure measured using the conventional PYSA and the photocatalytic activity have been reported by Yamagishi et al.,7 Song et al.,8 Miyamura et al.,9 and Fukumoto et al.10 On the other hand, the high wettability of the TiO₂ surface has been extensively studied,11–17 and has attracted considerable attention. Therefore, a newly designed PYSA was applied in order to evaluate the change in the TiO₂ surface depending upon the humidity. A significant change in the photoemission yield spectra due to exposure to a dry atmosphere was observed, which was explained by the desorption of water adsorbed on TiO₂.

Experimental

Apparatus

The experimental setup of a PYSA equipped with a dry attachment is shown in Fig. 1. UV-rays emitted from a deuterium lamp were monochromatized by a grating monochrometer (Model CT-10, JASCO) and focused on a sample surface via an optical fiber. Here, the energies of monochromatized UV-rays were shifted at 0.1 eV intervals up to 6.20 eV, because UV-rays with energies greater than 6.20 eV are greatly absorbed by O₂. The sample and the counting system were placed in a glovebox. The counting system is constructed with an open counter and a control circuit. The number of
emitted photoelectrons from the sample surface was counted by the open counter in air. The number of counter pulses per second produced at the anode is a function of the number of electrons emitted from the sample. A loss of counts is, however, introduced during the dead time of the counter. Thus, the number of electrons entered into the counter per second is expressed by the following equation:

\[ N_{\text{in}} = N_{\text{em}} f \tau / (1 - \tau N_{\text{obs}}) \]  

(1)

Here, \( N_{\text{em}} \) is the number of electrons emitted from the sample per second, \( f \) the fraction of electrons entered into the counter, \( \tau \) the dead time and \( N_{\text{obs}} \) the number of observed electrons per second. The photoemission yield is derived by dividing \( N_{\text{em}} \) by the number of incident photons, which are counted using a photodiode (Model S1227-1010BQ, Hamamatsu Photonics) placed at a sample position.

The counting character of the open counter is sensitive to any changes in the humidity and the temperature. A high humidity leads to high counting rates due to surface leakage of the counter. Therefore, the space inside the counter was filled with dry air and kept at the same humidity during measurements. In addition, the temperature inside the counter was kept constant at 25°C.

**Drying procedure**

At first, the main chamber is purged with dry compressed air for 15 min. Dry compressed air is introduced into the main chamber through the inlet at a constant flow rate (2 liter/min), and is discharged through the outlet. Then, the inlet and outlet are closed. Moisture in the main chamber is removed by continuously circulating through the gas purifier (Model DGE-45, UNICO). The gas purifier uses a molecular sieve, which removes moisture from the gas that passes through it. The moisture content was monitored as the dew point by a hygrometer (Model TK-100, TEKHNE) mounted in the gas stream piping. All samples are passed in and out of the main chamber on a sliding tray installed in the antechamber without disturbing the main chamber atmosphere.

**Sample**

Commercially available high-purity powders of polycrystalline TiO\(_2\) with the anatase structure (KOJUNDO CHEMICAL LABORATORY, 99%) were employed.

**Results and Discussion**

The dew point of atmosphere in the main chamber fell to –20°C upon purging with dry compressed air for 15 min. Figure 2 shows the dew point of the atmosphere in the main chamber as a function of the circulation time. As can be seen from Fig. 2, the dew point of the atmosphere in the main chamber fell to –30°C after circulation for 35 min, and fell to –40°C after circulation for 190 min. When the main chamber was empty without any samples in it, the dew point fell to –40°C after circulation for 40 min. Concerning the photoemission yield measurement, the sample was introduced when the dew point was –40°C. Although the dew point increased up to –35°C, due to sample introduction, it returned to –40°C within approx. 30 min. After that, the dew point remained at –40 ± 0.5°C.

Photoemission yield spectra of TiO\(_2\) (anatase) were taken as a function of the duration of exposure to a dry atmosphere. Typical data recorded just after exposure to a dry atmosphere and after 360 min of exposure to a dry atmosphere were shown in Fig. 3. The threshold energy of the photoemission, \( E_{\text{PET}} \), which corresponds to the first photoionization potential, was determined from the...
energy of an intersecting point between a background line and the extended line of the cube root of the photoemission yield. Based on Fowler’s analysis, the square root of the photoemission yield is usually applied for metals. On the other hand, for semiconductors the cube root of the photoemission yield is usually applied based on Kane’s theory. Here, the cubic root of the photoemission yield showed good linearity, and was applied for the determination of $E_{\text{PET}}$. The slope of the extended line represents the photoelectron emission rates. As can be seen in Fig. 3, the differences in $E_{\text{PET}}$ and in the slope are remarkable. In Fig. 4, the observed $E_{\text{PET}}$ and slopes are plotted as a function of the exposure duration to the dry atmosphere. The gradual decrease of $E_{\text{PET}}$ and the increase of the slope were observed for up to 200 min. In addition, after 8 h of exposure to a wet atmosphere (25°C, 50%RH), we confirmed that $E_{\text{PET}}$ and the slopes of the sample exposed to dry atmosphere returned to initial values. The results of the samples without any exposure to the dry atmosphere are also shown in Fig. 4. It was confirmed that the change in the PYS was caused by exposure to a dry atmosphere; also, the influence of UV irradiation during the measurement was confirmed to be negligibly small. The photoelectrons emitted from the surface of TiO$_2$ were detected after passing the layer of adsorbed water. Therefore, the number of the photoelectrons that can reach the counter depends on the layer thickness of adsorbed water. If the layer of adsorbed water becomes thinner under a dry atmosphere, the number of photoelectrons increases. To elucidate these results, we also observed the change in the photoemission yield spectra caused by the thermal desorption of adsorbed water. According to a temperature programmed desorption study, the water physically adsorbed on TiO$_2$ surface was desorbed by heating at 69 – 127°C. During the PYS measurement, the sample temperature was kept in air at 80°C. Figure 5 shows the changes in $E_{\text{PET}}$, and that the slopes of $Y$ vary with the heating time. The influence of heating on the sensitivity of the open counter should be noted here. The result of a sample measured for confirmation is also shown in Fig. 5. It was kept at 80°C outside the instrument, and measured on the usual sample stage at 25°C. This result suggests that the influence of heating on the sensitivity of the open counter can be neglected. The trends in concerning $E_{\text{PET}}$ and the slope are consistent with those obtained by exposure to a dry atmosphere. Because the physisorbed water on the TiO$_2$ surface was gradually desorbed by heating, the $E_{\text{PET}}$ decreased and the slope of $Y$ increased. This suggests that the change in the photoemission yield spectra obtained using FYSA equipped with the dry atmosphere attachment is caused by the desorption of adsorbed water on the TiO$_2$ surface.

When the surface is covered with another layer, e.g. oxides on Si$^2$ and n-alkylmercaptanes on Au$^3$, a plot of $\ln(Y)$ against the thickness of the layer shows a straight line. Therefore, $\ln(Y)$ is expressed by a following equation:

$$\ln(Y) = -\alpha T + C. \quad (2)$$

Here, $T$ is the thickness of the layer, $C$ a constant ($\ln(Y)$ for $T = 0$), $\alpha$ a coefficient dependent on the kinetic energy of the
Table 1 Table of results for the slope (m) and linearity (r²) of ln(S') and Dₜ

|         | m  | r²  |
|---------|----|-----|
| first-order | -2.34 | 0.988 |
| second-order | -2.52 | 0.998 |

When the photoemission yield shows the maximum, and the obtained photoemission yield is minimum. On the other hand, when the photoemission yield shows the maximum (t > 200 min), the thickness is minimum. Changes in the thickness of the layer of adsorbed water are expressed as the decay ratio, Dₜ:

\[
Dₜ = (T(t) - T_{min})(T_{max} - T_{min}),
\]

where \(T(t), T_{min}\) and \(T_{max}\) are the instantaneous, minimal and maximal thickness, respectively. In this study, Eq. (2) was converted to the following equation using the slope of \(Y\) which characterizes the escape probability of electrons from the surface;

\[
\ln(S') = -mDₜ + C'.
\]

Here, \(S\) is the slope of \(Y\), and \(C'\) a constant (\(\ln(S')\) for \(T(t) = T_{min}\)).

Next, we try to apply first- or second-order reaction rate equation to the time dependence of the change in the thickness of the layer of adsorbed water, as follows;

\[
\frac{dT}{dt} = k_1 T,
\]

\[
\frac{dT}{dt} = k_2 T^2,
\]

where \(k_1\) and \(k_2\) are the rate constants. \(k_1\) and \(k_2\) are deduced by maximizing the correlation coefficient (\(r^2\)) of the plot of \(\ln(S')\) against \(Dₜ\). The results are presented in Table 1. Here, the average of 3 replicates is used as \(S\). As shown in Fig. 6, the plot of \(\ln(S')\) against \(Dₜ\), estimated from the second-order equation, shows good linearity, indicating that Eq. (6) is a good representation of the time dependence of the change in the thickness of the layer of adsorbed water. The changes in \(E_{PET}\) and the slopes of \(Y\) under a dry atmosphere are almost explained by the change in the thickness of the layer of adsorbed water. Of course, it is also considered that \(E_{PET}\) reflects the changes in the surface electronic structures owing to the adsorption of water. However, a detailed analysis is difficult only from these data.

Conclusions

We have investigated the change in the photoemission yield spectra caused by the desorption of water adsorbed on the TiO₂ surface. We prepared a new type of PYSA equipped with dry atmosphere attachment using a glovebox.

As an increment of the duration of exposure to the dry atmosphere, the threshold energy of the photoemission decreases and the photoelectron emission rate increases. It is derived from the fact that the layer of adsorbed water becomes thin under a dry atmosphere. These facts were confirmed by the thermal desorption of adsorbed water. On the other hand, the second-order reaction rate equation was applied to the time dependence of the change in thickness of the layer of adsorbed water.

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