Real-time Observation of Interface Atomic Structures by an Energy-Dispersive Surface X-ray Diffraction

Tetsuroh Shirasawa†

National Metrology Institute of Japan (NMIJ), National Institute of Advanced Industrial Science and Technology (AIST), Tsukuba, Ibaraki 305-8565, Japan
† Corresponding author: t.shirasawa@aist.go.jp

Received: 26 July, 2019; Accepted: 5 September, 2019; Published: 21 September, 2019

Surface X-ray diffraction is a powerful tool for studying the atomic structure of buried interfaces nondestructively. The analysis is often limited to the static structures, since the acquisition of crystal truncation rod (CTR) profile dataset is lengthy. Recently, high-speed methods have been developed by several groups, aiming for the in operando study of interface phenomena. Our method uses energy-dispersive convergent X-rays and area detector, and allows the quantitative structure analysis during irreversible phenomena in a typical time frame of 1 s. In this review, the energy-dispersive method is compared with the other high-speed methods which use high-energy X-rays with a grazing incidence geometry and transmission geometry, and then two examples of the real-time monitoring are presented, the photo-induced wettability transition of the rutile-TiO$_2$(110) surface and an electrochemical reaction on the Pt(111) electrode surface, to show the capability of the energy-dispersive method.

Keywords X-ray scattering, diffraction, and reflection; Surface structure, morphology, roughness, and topography; Surface chemical reaction; Single crystal surfaces; Metal-electrolyte interfaces

I. INTRODUCTION

Methods for characterizing interface properties under (nearly) practical sample conditions and environments have been developed for decades, aiming for the in operando observation of technologically relevant phenomena such as catalysis, electrochemical reactions, and battery reactions. Many fundamental aspects of the interface phenomena have been revealed by the operando techniques [1−4], however, many dynamical properties remain to be clarified probably due to the technical difficulty in capturing the interface phenomena with a sufficient temporal resolution.

Surface X-ray diffraction (SXRD) is one of the most reliable methods for studying interface structure [5−7]. The surface diffraction rods [crystal truncation rod (CTR) and fractional-order rod (FOR)] appearing in the direction perpendicular to the surface [e.g. Figure 1(a)] can provide the atomic structure across the interface with an accuracy of 10$^{-2}$−10$^{-1}$ Å under various sample environments without a destructive sample preparation, which is an unique ability and can be a big advantage over other techniques such as electron diffractions and microscopies.

A drawback of SXRD is that the measurement of diffraction rod profile is lengthy, and thus not suited to time-resolved measurements. In the conventional method, a monochromatic collimated X-ray beam is used and a diffraction rod profile is measured point-by-point with the rotation of the sample and detector. A typical data acquisition time is several hours or more, even when a third-generation synchrotron source is used. Recent progress in photon-counting position-sensitive area detector allows faster measurements; the rocking-curve measurement necessary to obtain the integrated intensity at each point of the diffraction rod can be omitted when a sufficiently large area detector is used [8]. However, the data acquisition time for a diffraction rod is still tens of minutes or more, which is in many cases longer than the relaxation time of interface phenomena.

Given this situation, high-speed SXRD methods have
been developed by several groups. Gustafson et al. adopted a grazing-incidence reflection geometry with high-energy monochromatic X-rays and a large area detector [9, 10]. (b) A transmission method with high-energy monochromatic X-rays and an area detector [13]. (c) An energy-dispersive method with an energy-dispersive convergent X-rays and an area detector [16].

We have developed a method that can measure a CTR profile in a single acquisition with the time resolution as short as 1 s [16]. This method uses an energy-dispersive convergent X-ray beam and an area detector and is capable of measuring a range of CTR profile simultaneously without moving anything [Figure 1(c)]. The basic concept is to use an energy-dispersive X-rays in stead of the incident angle scan: given that the momentum transfer along the surface normal direction is $Q_z = 4\pi \sin \theta / \lambda$ in the specular reflection geometry, the scattering profile along $Q_z$, i.e., the CTR profile, can be simultaneously measured by the dispersion of X-ray wavelength $\lambda$ even when the glancing angle $\theta$ is fixed. The single-acquisition CTR data allows the quantitative determination of the out-of-plane atomic structure, which is a big advantage over the high-energy monochromatic methods described above. In this review, two examples are presented to demonstrate the capability for the time-resolved quantitative structure analysis: the photo-induced wettability transition of the rutile-TiO$_2$(110) surface [17] and an electrochemical reaction on the Pt(111) electrode surface [18].

II. ENERGY-DISPERSIVE SXRD

A. Instrumentation

A schematic illustration of the experimental layout and photographs of the diffractometer and curved crystal polychromator, dedicated to the energy-dispersive method, are shown in Figure 2. The experiments were performed at beamline NW2A of the Photon Factory Advanced Ring (PF-AR) at KEK. The heart of this method is to generate the energy-dispersive (polychromatic) convergent X-ray beam.
from synchrotron white X-rays by using a curved crystal polychromator. Such a polychromatic beam was invented by Matsushita et al. for the high-speed measurement of X-ray absorption fine structure (XAFS) spectrum [19], and we adopted it to the SXRD measurements. Detailed characteristics of the polychromatic beam for the SXRD measurements is described elsewhere [16]. The polychromatic beam has a one-to-one relationship between the X-ray energy and the traveling direction, and thus the scattering intensity of each energy component is recorded at different positions of the area detector (PILATUS-100K, DECTRIS Ltd.). In the previous energy-dispersive method, a collimated white X-ray beam was used and the scattering profile was measured by a silicon drift detector (SDD) as a function of X-ray energy [20]. The resolution of the momentum transfer \( \Delta Q \) was limited by the energy resolution of SDD, and eventually the resolution was on the order of \( 10^{-1} \) Å\(^{-1} \) [20], which was not sufficient for the quantitative analysis. In the present method, \( \Delta Q \) is mainly determined by the pixel element size of the area detector and the sample–detector distance [16]. In the present conditions, the pixel element size was 0.172 mm and sample–detector distance was 500–1000 mm, and the resulting \( \Delta Q \) is smaller than \( 5 \times 10^{-3} \) Å\(^{-1} \), which is sufficient for the quantitative analysis.

We used a tapered undulator X-ray source in order to use a high-flux polychromatic beam with a smooth spectrum [21]. Two flat Rh-coated mirrors were used to eliminate higher-order harmonics, and a flat-bent Rh-coated mirror was used for vertical focusing. The mirror system was located upstream of the experimental hutch. The polychromator was a double-side-polished Si wafer with a thickness of 0.1 mm, which was elastically bent by the bender [Figure 2(c)], and the Si 111 reflection was used in the transmission geometry. The energy range of the polychromatic beam was 16–23 keV; in this energy range the radius of curvature of the polychromator \( \rho \) was \( \sim 425 \) mm. The highest energy cut-off was determined by the Rh K-absorption edge. The beam size at the sample position was 0.15 mm (FWHM) in both the vertical and horizontal directions. The sample goniometer and detector goniometer were mounted on a rotatable table whose rotational axis was on the rotational center of the polychromator, so that these goniometers can be rotated with respect to the direction of the polychromatic beam and can cover a range of the reciprocal space spanned by the X-rays. To obtain a quantitative CTR profile data, the measured CTR spectrum was normalize with the polychromatic beam spectrum.

**B. Fast measurements of CTR and RSM**

An example of single-acquisition CTR profile is shown in Figure 3(a). The sample was a GaAs/AlAs superlattice grown on a GaAs(001) substrate: 50 alternate stacks of 12 GaAs (3.39-nm thick) and 8 AlAs (2.26-nm thick) monolayers [inset of Figure 3(a)]. The black symbols represent the specular CTR profile measured by the conventional angle scan method with monochromatic X-rays of 9.5 keV (BL–4C of Photon Factory at KEK); the data acquisition time was about 3 h. The energy-dispersive method covered the same \( Q \) range in a single frame with an exposure time of 10 s (red symbols). The agreement with the conventional CTR profile data illustrates the quantitative measurement.

The energy-dispersive method is also useful for reciprocal space map (RSM) measurements which have been used for the study of shape, size, and orientation of crystalline domains of thin films [22]. The line profile in the area detector image, as indicated by the dashed line in the lower right panel of Figure 3(b), corresponds to the CTR profile, and the whole scattering distribution represents a two-dimen-
sional (2D) projection of RSM [16]. The 2D RSM of the left panel of Figure 3(b) was obtained from the single image acquired in 1 s, which is much faster in time and wider in Q range as compared to that obtained by the conventional point-by-point scan [upper right panel of Figure 3(b)]. It can be a powerful tool for the time-resolved study of thin films. Another approach for high-speed RSM acquisition developed by other groups is the so-called on-the-fly scan, in which multiple measurements were carried out during continuous rotation of a goniometer axis [23, 24]. It can acquire a 3D RSM in 10−100 s.

III. MONITORING INTERFACE PHENOMENA

I show two examples of the real-time monitoring of irreversible interface phenomena, demonstrating the capability of capturing the atomic structures within 1 s.

A. Photoinduced wettability transition of rutile-TiO$_2$(110) surface

Ultraviolet (UV) illumination can change a hydrophobic TiO$_2$ surface to a superhydrophilic surface [Figure 4 (a)]; the wettability transition was discovered in the late 1990s [25, 26]. While the wettability transition has been used for coating applications such as anti-fog, self cleaning, and heat dissipation coatings [27, 28], the mechanism remains to be clarified. A number of studies were devoted to understand the underlying atomic scale processes, and the opinions have been split into two groups. Several groups claimed that the photocatalytic decomposition of surface impurities results in the superhydrophilicity [29−34]. The other group claimed that a photoinduced intrinsic structural change of the TiO$_2$ surface leads to the superhydrophilicity [28, 35−40]. The controversy would arise from difficulties in the real-time observation of the atomic scale processes during the wettability transition. Vacuum-based surface analysis tools are often inadequate for such a study, because the surface processes in vacuum would be different from those in ambient conditions, and furthermore, it is known that the superhydrophilic surface is metastable and rapidly recovers to the hydrophobic surface in vacuum [41]. Theoretical studies are also challenging because the energy hierarchy of the water adsorption phases depends on the calculation conditions [42, 43]. We studied the possible structural change of the TiO$_2$ surface during the wettability transition in an ambient condition by SXRD measurements [17]. We studied the rutile-TiO$_2$(110) surface, as it has the lowest surface energy among the TiO$_2$ polymorphs surfaces [44].

Figure 4: (a) The hydrophobic and photoinduced superhydrophilic states of the rutile-TiO$_2$(110) surface. (b) Time evolutions of the CTR intensity in the (01L) rod during the UV illumination (λ = 365 nm, 87 mW cm$^{-2}$). (c) Measured (symbols) and calculated (solid and dashed lines) CTR profiles of the (10L) rod of the hydrophobic and superhydrophilic surfaces [17]. The diffraction indices (HKL) are based on the surface lattice unit cell of $a = c = \sqrt{2}a_0 = 6.4972$ Å and $b = c_0 = 2.9587$ Å, where $a_0$ and $c_0$ are the tetragonal lattice constants of the bulk crystal.

Time-resolved measurements in the energy-dispersive Scattering amplitude [a.u.]

| UV illumination time [s] | Normalized CTR intensity |
|-------------------------|--------------------------|
| 0                       | 1.0                      |
| 200                     | 1.5                      |
| 400                     | 2.0                      |
| 600                     | 1.5                      |
| 800                     | 1.0                      |

(b) Normalized CTR intensity

(c) Scattering amplitude [a.u.]

Figure 5: A possible mechanism of the photoinduced wettability transition of the rutile-TiO$_2$(110) surface [17]. (a) The hydrophobic surface is covered with O atom (O$_T$) located atop the five-coordinate Ti atom, bridging O atom (O$_B$), and ordered adsorbed water molecule (AW). (b) UV illumination induces the proton transfer from the O$_T$ site to the O$_B$ site. (c) The resulting OH groups at the O$_T$ and O$_B$ sites can be active sites for the water adsorption due to an increased number of hydrogen bonds (dashed lines).
mode demonstrated the structural change of the rutile-
TiO$_2$(110) surface during the UV illumination in a humid
condition. Figure 4(b) displays time evolutions of the scat-
tering intensity at different positions of (01L) rod during the
UV illumination ($\lambda = 365$ nm, 87 mW cm$^{-2}$), showing the
intensity changes in a few hundred seconds. The time scale
is similar to that of the change spanning water contact angle
[35], indicating that the surface structural change is associ-
ated with the wettability transition. Figure 4(c) shows the
intensity profiles of (10L) rod measured before and after the
UV illumination. The significant change in the profile
clearly indicates an atomic scale structural change. No sig-
nificant intensity change was observed when the UV-light
power was less than 20 mW cm$^{-2}$, consistent with the UV-
power threshold for the wettability transition [35].

The atomic structures of the hydrophobic and superhy-
drophilic surfaces were quantitatively analyzed using static
CTR data [17]. The atomic positions and Ti–O and O–O
bond lengths indicate that, on the hydrophobic surface, the
two-coordinated Ti atom was terminated with an O atom
[denoted as O$_T$ in Figure 5(a)] which is likely in a form of
water, the bridging O atom (O$_B$) were not hydroxylated, and the surface was partially covered with adsorbed water mol-
ecules (AW) located at a lattice site (the site occupancy was
~0.3). These features are consistent with the previous CTR
study on the surface immersed in water [45] and first-princi-
ples calculations [42, 46]. On the superhydrophilic surface,
large positional fluctuations were found for O$_T$, O$_B$, and the
topmost TiO layer, and the ordered AW layer was lifted.

Based on the determined atomic structures and chemical
states provided by previous reports, we proposed a mecha-
nism of the wettability transition as shown in Figure 5 [17].
The UV illumination can induce a proton transfer from the
intact water at the O$_T$ site to the non-hydroxylated oxygen at
the O$_B$ site [47] [Figure 5(b)]. The resulting surface OH
groups at the O$_T$ and O$_B$ sites can be active sites for the wa-
ter adsorption because the number of hydrogen bonding is
increased [Figure 5(c)]. The neighboring OH groups at the
O$_T$ and O$_B$ sites can form hydrogen bond with each other,
which may cause a large positional displacement from the
lattice sites [48]. The displacement can induce a local lattice
strain in the underlying TiO$_2$ layers, as indicated by the large
positional fluctuation of O$_T$, O$_B$, and the topmost TiO layer
in the determined structure. The AW might be disordered
due to the structural fluctuation of the surface, and eventu-
ally they are invisible in the diffraction data. It is known that
the superhydrophilic surface consists of hydrophobic and
hydrophilic domains with several tens of nanometer in size
[25, 26]. We speculated that the formation of the domain
structure might be caused by a strain-relief mechanism: the
lattice strain generated in the hydrophilic domain can be
released in the hydrophobic domain. I note that very recent-
ly a CTR study suggests that the superhydrophilicity is
cased by the depletion of surface carbon contamination
coupled to an extensive surface hydroxylation [49]. A com-
bination of structural analysis and chemical composition
analysis in ambient conditions is strongly required to clarify
the mechanism.

B. Electrochemical decomposition of Meth-
anol on Pt(111) electrode

Many elementary steps are involved in an electrochemical
reaction on the electrode surface, such as the adsorption of
reactant molecules, diffusion, decomposition, formation of
intermediate states and final product, and desorption. Con-
siderable insights of the elementary steps have been provid-
ed by novel in situ techniques on well-defined crystalline
electrode surfaces [2, 3, 50]. SXRD has played a central role
for the structure analysis of electrochemical interfaces
[51–53]. In previous studies, structural changes of electrode
surfaces, such as the creation/destruction of surface super-
structures [54, 55] and surface oxidation [56] and etching
[57] of electrodes, were studied by monitoring a specific
point of a diffraction rod. However, such a single-point
monitoring can be insufficient for the quantitative structure
analysis.

We studied the structural change of a Pt(111) single-
crystal electrode surface during electrochemical decomposi-
tion of methanol. The reaction is the basis of the direct
methanol fuel cells. The overall reaction is described as
CH$_3$OH + H$_2$O $\rightarrow$ CO$_2$ + 6H$^+$ + 6e$^-$, however, in reality the reaction consists of intermediate states [58]. The dominant
inertive intermediate state is the so-called CO poisoning
layer. Methanol is decomposed into CO immediately after
the adsorption on a Pt surface, CH$_3$OH $\rightarrow$ CO$_{ads}$ + 4H$^+$ + 4e$^-$, where the subscript “ads” indicates that the species is
adsorbed on the surface. The CO$_{ads}$ covers most part of the
Pt surface, and the catalytic activity for the methanol de-
composition is significantly reduced. The CO$_{ads}$ layer is fi-
nally desorbed from the surface when oxygen species are
adsorbed on the surface, via CO$_{ads}$ + OH$_{ads}$ $\rightarrow$ CO$_2$ + H$^+$ + e$^-$. We studied the kinetics of CO poisoning by using the
energy-dispersive CTR measurements. Details of the ex-
perimental setup is described elsewhere [18].

We measured the specular CTR profile of the Pt(111)
electrode while changing the potential applied to the Pt(111)
electrode, and every CTR profile was analyzed. Figure 6(a)
shows the vertical displacement of the Pt surface layer (Δz)
obtained by the time-resolved analysis, and Figure 6(b)
does the cyclic voltammogram (CV) simultaneously
measured. A clear correlation between the structural change
and reaction current can be seen. We note that the analysis
could not identify the adsorbed molecules due probably to
their much weaker X-ray scattering and likely to their struc-
tural inhomogeneity as compared to Pt. In the positive-going
potential scan, in the potential region of 0.0–0.4 V [vs. re-
vissible hydrogen electrode (RHE)] most part of the surface
was covered with the CO$_{ads}$ and the reaction current was
quite small [59]. The Pt surface layer was lifted up to about
0.11 Å due to the strong interaction between CO$_{ads}$ and Pt
[60]: the value of Δz coincides with that of the Pt(111)-(2×2)-3CO ordered structure [61]. When the potential
was increased above 0.6 V, the Pt surface layer was relaxed and
the oxidation current increased simultaneously, demonstrating the oxidative desorption of CO$_{ads}$. In the negative-going scan, the $\Delta z$ increased in the potential region of 0.8−0.4 V due to the readsorption of CO$_{ads}$. An important point is that, the structural change shows the hysteresis in the potential region of 0.5−0.7 V, which is well correlated with the hysteresis in CV. The hysteresis became larger when the potential scan rate was increased to 50 mV s$^{-1}$ [Figure 6(c, d)]. The results clearly demonstrate that the stripping of the CO$_{ads}$ layer is the rate-determining step of the methanol decomposition.

The kinetics of CO$_{ads}$ desorption was studied by using potential step experiments. Figure 7 shows the time evolution of the structural change after the potential step from 0.0 V to 0.8 V. After the potential step, the $\Delta z$ gradually decreased due to the CO$_{ads}$ layer stripping. Taking a close look at the initial change (highlighted region), interestingly, the $\Delta z$ did not decrease for about 5 s after the potential step; it rather increased from the initial value. A similar behavior was observed in the potential scan experiments (Figure 6): in the positive-going scans the $\Delta z$ slightly increases at ca. 0.4 V with the slight increases in reaction current and then decreases at ca. 0.6 V and 0.8 V in Figures 6(a) and 6(c), respectively. The behavior is not compatible with a simple model for the CO$_{ads}$ desorption, a continuous decrease of the CO$_{ads}$-covered area during the CO$_{ads}$ desorption, but can be explained by the formation of a more strongly adsorbed less-dense CO$_{ads}$ layer. It was suggested that the CO$_{ads}$ oxidation is initiated at active sites such as step edges [62]. The CO$_{ads}$ molecules at surface terrace would diffuse toward the active sites [63] in order to compensate the concentration gradient, and thus the less-dense CO$_{ads}$ layer is temporarily formed on the terrace. According to first-principles calculations, the CO−Pt interaction becomes stronger when the CO$_{ads}$ density is reduced due to the suppression of the repulsive intermolecular interaction [64]. Therefore, the increase in $\Delta z$ reasonably indicates the formation of less-dense strongly adsorbed CO$_{ads}$ layer. Previous time-resolved infrared spectroscopy measurements suggested the existence of strongly adsorbed CO$_{ads}$ layer [65]. Our time-resolved structure analysis demonstrated its existence more clearly.

### IV. SUMMARY

The capability of energy-dispersive SXRD technique for capturing interface phenomena is presented. This method allows a CTR profile to be measured at once in 1 s or less, which can be hundreds times faster than the conventional monochromatic angle-scan method, realizing quantitative atomic scale structure analysis in the time frame. Besides the two examples presented here, we applied this method to the real-time monitoring of thin film growth and succeeded in capturing atomic scale processes during the growth. We will also apply this method to all-solid-state battery interfaces and catalyst surfaces. A possible upgrade of this method is an energy-dispersive small angle X-ray scattering which would realize a simultaneous analysis of element-specific local atomic structure and shape and size of nano particles; it would be a powerful tool for the in operando studies of practical complex systems.

---

**Figure 6**: Vertical displacement of the surface atomic layer of the Pt(111) electrode during the potential scan in the methanol solution (0.5 M CH$_3$OH/0.1 M HClO$_4$) and the simultaneously measured CV [18]. (a, b) The potential scan rate was 5 mV s$^{-1}$. (c, d) The potential scan rate was 50 mV s$^{-1}$.

**Figure 7**: Time evolutions of the vertical displacement of the surface atomic layer of the Pt(111) electrode (upper panel) and reaction current (lower panel) after a potential step from 0.0 V to 0.8 V in the methanol solution [18].
Acknowledgments

The development of energy-dispersive SXRD diffractometer was supported by JST, PRESTO (Grant Number JPMJPR13C5). The author appreciates the technical supports from Kohei Uosaki and Takuya Masuda for the electrochemical experiments.

References

[1] J. Y. Park (Ed.), Current Trends of Surface Science and Catalysis (Springer, New York, 2014).
[2] A. Wiecekowski (Ed.), Interfacial Electrochemistry: Theory, Experiment, and Applications (Marcel Dekker, New York, 1999).
[3] T. Masuda and K. Uosaki, in: Electrochemical Science for a Sustainable Society: A Tribute to John O'M Bockris, edited by K. Uosaki (Springer, Cham, 2017) p. 147.
[4] F. Lin, Y. Liu, X. Yu, L. Cheng, A. Singer, O. G. Shpyrko, H. L. Xin, N. Tamura, C. Tian, T.-C. Weng, X.-Q. Yang, Y. S. Meng, D. Nordlund, W. Yang, and M. M. Doeff, Chem. Rev. 117, 13123 (2017).
[5] R. Feidenhans’l, Surf. Sci. Rep. 10, 105 (1989).
[6] I. K. Robinson, in: Handbook on Synchrotron Radiation, Vol. 6, edited by G. Brown and D. Moncton (Elsevier, Amsterdam, 1991) Chap. 7.
[7] T. Shirasawa and T. Takahashi, in: Reference Module in Chemistry, Molecular Sciences and Chemical Engineering (Elsevier, 2014).
[8] C. M. Schlepütz, R. Herger, P. R. Willmort, B. D. Patterson, O. Bunk, Ch. Brönnimann, B. Henrich, G. Hülsen, and E. F. Eikenberry, Acta Crystallogr. A 61, 418 (2005).
[9] C. Nicklin, Science 343, 739 (2014).
[10] J. Gustafson, M. Shipilin, C. Zhang, A. Stierle, U. Hejral, U. Ruet, O. Gutowski, P.-A. Carlsson, M. Skoglundh, and E. Lundgren, Science 343, 758 (2014).
[11] T. Takahashi, S. Nakatani, N. Okamoto, T. Ishikawa, and S. Kikut, Surf. Sci. 242, 54 (1991).
[12] H. Tajiri, O. Sakata, and T. Takahashi, Appl. Surf. Sci. 234, 403 (2004).
[13] F. Reikowski, T. Wiegmann, J. Stettner, J. Dmec, V. Honkimäki, F. Maroun, P. Allongue, and O. M. Magnusson, J. Phys. Chem. Lett. 8, 1067 (2017).
[14] U. Hejral, P. Müller, O. Balmes, D. Pontoni, and A. Stierle, Nat. Commun. 7, 10964 (2016).
[15] U. Hejral, P. Müller, M. Shipilin, J. Gustafson, D. Franz, R. Shaydul, U. Rütt, C. Zhang, L. R. Merte, E. Lundgren, V. Vonk, and A. Stierle, Phys. Rev. B 96, 195433 (2017).
[16] T. Matsuhashita, T. Takahashi, T. Shirasawa, E. Arakawa, H. Toyokawa, and H. Tajiri, J. Appl. Phys. 110, 102209 (2011).
[17] T. Shirasawa, W. Voegeli, E. Arakawa, T. Takahashi, and T. Matsuhashita, J. Phys. Chem. C 120, 29107 (2016).
[18] T. Shirasawa, T. Masuda, W. Voegeli, E. Arakawa, C. Kamezawa, T. Takahashi, K. Uosaki, and T. Matsuhashita, J. Phys. Chem. C 121, 24726 (2017).
[19] T. Matsuhashita and R. P. Phizackerley, Jpn. J. Appl. Phys. 20, 2223 (1981).
[20] K. Ellmer, R. Mientus, V. Weiß, and H. Rossner, Meas. Sci. Technol. 14, 336 (2003).
[21] S. Yamamoto, K. Tsuchiya, and T. Shiioy, AIP Conf. Proc. 705, 235 (2004).
[22] U. Pletsch, V. Holý, and T. Baumbach, High-Resolution X-Ray Scattering from Thin Films to Lateral Nanostructures (Springer, New York, 2004).
[23] W. Hu, H. Suzuki, T. Sasaki, M. Kozu, and M. Takahasi, J. Appl. Crystallogr. 45, 1046 (2012).
[24] Z. L. Luo, H. Huang, H. Zhou, Z. H. Chen, Y. Yang, L. Wu, C. Zhu, H. Wang, M. Yang, S. Hu, H. Wen, X. Zhang, Z. Zhang, L. Chen, D. D. Fong, and C. Gao, Appl. Phys. Lett. 104, 182901 (2014).
[25] R. Wang, K. Hashimoto, A. Fujishima, M. Chikuni, E. Kojima, A. Kitamura, M. Shimohigoshi, and T. Watanabe, Nature 388, 431 (1997).
[26] R. Wang, K. Hashimoto, A. Fujishima, M. Chikuni, E. Kojima, A. Kitamura, M. Shimohigoshi, and T. Watanabe, Adv. Mater. 10, 135 (1998).
[27] H. Irie, K. Sunada, and K. Hashimoto, Electrochemistry 72, 807 (2004).
[28] K. Hashimoto, H. Irie, and A. Fujishima, Jpn. J. Appl. Phys. 44, 8269 (2005).
[29] J. M. White, J. Szanyi, and M. A. Henderson, J. Phys. Chem. B 107, 9029 (2003).
[30] J. T. Yates, Jr., Surf. Sci. 603, 1605 (2009).
[31] T. Zubkov, D. Stahl, T. L. Thompson, D. Panayotov, O. Diwald, and J. T. Yates, Jr., J. Phys. Chem. B 109, 15454 (2005).
[32] T. L. Thompson and J. T. Yates, Jr., Chem. Rev. 106, 4422 (2006).
[33] N. Ohtsu, N. Masahashi, Y. Mizukoshi, and K. Wagatsura, Langmuir 25, 11586 (2009).
[34] N. Ishida and D. Fujita, J. Vac. Sci. Technol. A 30, 051402 (2012).
[35] R. Wang, N. Sakai, A. Fujishima, T. Watanabe, and K. Hashimoto, J. Phys. Chem. B 103, 2188 (1999).
[36] M. Miyauchi, A. Nakajima, A. Fujishima, K. Hashimoto, and T. Watanabe, Chem. Mater. 12, 3 (2000).
[37] N. Sakai, A. Fujishima, T. Watanabe, and K. Hashimoto, J. Phys. Chem. B 105, 3023 (2001).
[38] A. Nakajima, S. Koizumi, T. Watanabe, and K. Hashimoto, J. Photochem. Photobiol. A 146, 129 (2001).
[39] R.-D. Sun, A. Nakajima, A. Fujishima, T. Watanabe, and K. Hashimoto, J. Phys. Chem. B 105, 1984 (2001).
[40] N. Sakai, A. Fujishima, T. Watanabe, and K. Hashimoto, J. Phys. Chem. B 107, 1028 (2003).
[41] H. Irie and K. Hashimoto, in: Environmental Photochemistry Part II, edited by P. Boule, D. W. Buhmann, and P. K. J. Roberts (Springer, Berlin, Heidelberg, 2005) p. 425.
[42] L.-M. Liu, C. Zhang, G. Thornton, and A. Michaelides, Phys. Rev. B 82, 164145(R) (2010).
[43] L. Yang, D.-J. Shu, S.-C. Li, and M. Wang, Phys. Chem. Chem. Phys. 18, 14833 (2016).
[44] M. Ramamoorthy, D. Vanderbilt, R. D. King-Smith, Phys. Rev. B 49, 16721 (1994).
[45] Z. Zhang, P. Fenter, N. C. Sturchio, M. J. Bedzyk, M. L. Machesky, and D. J. Wesolowski, Surf. Sci. 601, 1129 (2007).
[46] T. Ohito, A. Mishra, S. Yoshimune, H. Nakamura, M. Bonn, and Y. Nagata, J. Phys. Condens. Matter 26, 244102 (2014).
[47] S. Tan, H. Feng, Y. Ji, Y. Wang, J. Zhao, A. Zhao, B. Wang, Y. Luo, J. Yang, and J. G. Hou, J. Am. Chem. Soc. 134, 9978 (2012).
[48] A. V. Bandura, D. G. Sykes, V. Shapovalov, T. N. Truong, J. D. Kubicki, and R. A. Evarestov, J. Phys. Chem. B 108, 7844 (2004).
[49] J. P. W. Treacy, Hussain, X. Torrelles, G. Cabailh, O. Bikon, C. Nicklin, G. Thornton, and R. Lindsay, J. Phys. Chem. C 123, 8463 (2019).
[50] C. Korzeniewski, V. Climent, and J. M. Feliz, in: Electroanalytical Chemistry: A Series of Advances, Vol. 24, edited by A. J.
Bard and C. G. Zoski (CRC Press, Boca Raton, Florida, 2012) Chap. 2.

[51] Z. Nagy and H. You, Electrochim. Acta 47, 3037 (2002).

[52] N. M. Marković and P. N. Ross Jr., Surf. Sci. Rep. 45, 117 (2002).

[53] K. Uosaki, Jpn. J. Appl. Phys. 54, 030102 (2015).

[54] I. M. Tidswell, N. M. Markovic, and P. N. Ross, J. Electroanal. Chem. 376, 119 (1994).

[55] K. Tamura, J. X. Wang, R. R. Adžić, and B. M. Ocko, J. Phys. Chem. B 108, 1992 (2004).

[56] H. You, D. J. Zurawski, Z. Nagy, and R. M. Yonco, J. Chem. Phys. 100, 4699 (1994).

[57] F. Golks, K. Krug, Y. Grünä, J. Zegenhagen, J. Stettner, and O. M. Magnussen, J. Am. Chem. Soc. 133, 3772 (2011).

[58] T. Iwashita, in: Handbook of Fuel Cells: Fundamentals, Technology and Applications, Vol. 2, edited by W. Vielstich, A. Lamm, and H. A. Gasteiger (John Wiley & Sons, New York, 2003).

[59] T. Iwashita, Electrochim. Acta 47, 3663 (2002).

[60] D. Curulla, A. Clotet, J. M. Ricart, and F. Illas, J. Phys. Chem. B 103, 5246 (1999).

[61] C. A. Lucas, N. M. Marković, and P. N. Ross, Surf. Sci. 425, L381 (1999).

[62] J. Inukai, D. A. Tryk, T. Abe, M. Wakisaka, H. Uchida, and M. Watanabe, J. Am. Chem. Soc. 135, 1476 (2013).

[63] H. Hanawa, K. Kunimatsu, H. Uchida, and M. Watanabe, Electrochim. Acta 54, 6276 (2009).

[64] J. A. Steckel, A. Eichler, and J. Hafner, Phys. Rev. B 68, 085416 (2003).

[65] G. Samjeské, K.-i. Komatsu, and M. Osawa, J. Phys. Chem. C 113, 10222 (2009).

All articles published on e-J. Surf. Sci. Nanotechnol. are licensed under the Creative Commons Attribution 4.0 International (CC BY 4.0). You are free to copy and redistribute articles in any medium or format and also free to remix, transform, and build upon articles for any purpose (including a commercial use) as long as you give appropriate credit to the original source and provide a link to the Creative Commons (CC) license. If you modify the material, you must indicate changes in a proper way.

Published by The Japan Society of Vacuum and Surface Science