Structure Determination of Self-Assembled Monolayer on Oxide Surface by Soft-X-Ray Standing Wave*  

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Normal incidence X-ray standing wave (NIXSW) method was applied to the determination of geometrical location of atoms in organic molecules on oxide surface. The system investigated was alkyl phosphonic acid (C₈H₁₇PO₃H) adsorbed on a sapphire surface, which is one of the candidate systems for self-assembled monolayer (SAM) on oxides. The sample surface was irradiated by synchrotron soft X-rays (λ: 0.3~0.6 nm) from the surface normal, and the intensities of photoelectrons were plotted as a function of the photon energy. As a result, we observed clear modulations of photoelectron intensity around 3050 eV due to the standing wave from the sapphire substrate. Compared with the simulation using the crystal parameters, it was found that the phosphorus atoms are located at 0.11 nm from the surface, while the constant height was not observed for carbon atoms. The results are in consistent with the observations by X-ray photoelectron spectroscopy (XPS) and near-edge X-ray absorption fine structure (NEXAFS) where the molecules form SAM on the sapphire surface through the phosphonic acid, while the alkyl chain is located at the upper side. The present results shed light on the further applications of NIXSW method to the structure analysis of atoms and molecules on insulating materials like oxides. [DOI: 10.1380/ejssnt.2012.69]

Keywords: Standing Wave; Oxide; Sapphire; XPS; NEXAFS

I. INTRODUCTION

Metal oxides are widely used as various surface functional materials such as catalyst, photo-catalyst, adsorbent, and substrates of semiconductor devices. The interaction between molecules and the oxide surface is one of the key problems in surface science for the development of new surface functional materials with high quality. Particularly it is of great importance to understand the structures and dynamics of molecules at oxide surfaces from a fundamental materials science perspective. The important issues are (1) the principles of formation of ordered interface layer between two entirely different materials, (2) electronic properties at the interface and the coupling of the two different materials, and (3) chemical bonding states at the interface. For the understanding of the above issues, geometrical structures must be firstly understood before electronic properties and chemical interaction mechanisms are clarified. For this purpose, the precise determination of the geometrical location of adsorbed atoms and molecules on the oxide surface is one of the key factors to be elucidated.

Up to now, various surface analytical techniques such as X-ray photoelectron spectroscopy (XPS), ultra-violet photoelectron spectroscopy (UPS), Auger electron spectroscopy (AES), and low energy electron diffraction (LEED) have been applied to the estimation of the geometrical location of atoms and molecules on solid surfaces. However, precise determination of geometrical location of atoms and molecules is difficult by these methods. In addition, for insulating oxides with wide band-gap, the application of the above methods is limited due to the charging effect induced by the electron emission. Ion scattering spectroscopy (ISS) is an alternative method that has been successfully applied to the determination of the geometrical location of atoms on oxide surfaces [1-3]. But the information obtained by ISS is limited and the irradiation of ion beams on adsorbed molecules causes serious damages.

An X-ray standing wave (XSW) method is known to be a powerful tool to determine the structure of single crystal surfaces [4]. Especially, normal incidence X-ray standing wave (NIXSW) using soft X-rays from synchrotron light source has excellent characteristic where the distance between adsorbed atoms and surface can be precisely determined [5]. The NIXSW has been successfully applied to the determination of geometrical locations of metallic atoms [6], adsorbed molecules [7-11], and self-assembled monolayer [12,13] on metallic single-crystals. In spite of the abovementioned importance of oxides as surface functional materials, the NIXSW has scarcely been applied to the surface structure analysis of insulating oxides. Kim et al. have applied the XSW measurements to the structure determination of the FeS₂ layer formed on Fe₂O₃ [14]. However, the determination of geometrical location for adsorbed atoms and molecules on wide-gap oxide surfaces has not been reported.

In this work, we present the first results for the geometrical determination of atoms and molecules adsorbed on a surface of insulating oxide with wide band-gap. The system investigated is decyl-phosphonic acid (DPA, C₁₀H₂₁PO₃H) adsorbed on a sapphire surface. This system was chosen in the following background.

Aluminum oxides as well as the other metal oxides are used in various organic semiconductor devices due to their insulating and transparent properties. The formation of

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well-ordered monolayer of organic molecules on oxide surfaces is one of the key technologies for the development of organic devices. Recently, we have found that alkyl-chain molecules terminated by some functional groups such as alkoxides [15] and phosphonic acids [16] form self-assembled monolayer (SAM) on oxide surfaces by a simple immersion method. In order to confirm the applicability of this simple method to the formation of stable SAM’s, the precise determination of the surface structure on the oxide is indispensable.

In the present paper, the applicability of the NIXSW method to the structure determination of oxide surface is firstly demonstrated using sapphire single crystal as a substrate. Then we will show the results for the geometrical determination of SAM on the sapphire surface by the NIXSW method. The results are compared with the observation by XPS and NEXAFS, and the surface geometrical structures of SAM on the sapphire surface are discussed.

II. EXPERIMENTAL

All the experiments were performed at the BL-27A station of the Photon Factory in the High Energy Accelerator Research Organization (KEK-PF). The X-rays were emitted from the bending magnet, and the photon energy was tuned by an InSb(111) double crystal monochromator. The photon energy of the beam lines covers from 1.8 keV to 4.2 keV, and the typical photon flux was $\sim 10^{10}$ photons-$cm^{-2}\cdot s^{-1}$. The energy resolution of the monochromator was 1.5 eV at 3000 eV.

The ultrahigh vacuum chamber (base pressure $1 \times 10^{-8}$ Pa) was equipped with a hemispherical electron-energy analyzer (VSW Co. Class-100) for XPS measurements. The sample was horizontally located, and it was rotated around the vertical axis.

A C(0001) face of a sapphire plate (Jiaozuo City Crystal Photoelectric Material Co., Ltd.) of $10 \times 10 \times 0.1$ mm was used as a substrate. The surface of sapphire was rinsed by supersonic waves in ethanol for 15 minutes. The molecules used were decyl-phosphonic acid (DPA, CH$_3$(CH$_2$)$_{9}$-PO$_3$, Tokyo Chemicals Industry Co., Ltd.). This molecule has saturated alkyl chain with ten carbon atoms, and the terminal carbon is bonded to phosphonic acid. The SAM sample was prepared by immersing the substrates in a liquid in the following procedure. Firstly, the sapphire plate was immersed in distilled water, then it was immersed in 0.01 Mol/dm$^3$ of DPA-ethanol liquid for 20 hours. Then the substrate was rinsed by supersonic waves in ethanol for 15 minutes, and dried in atmosphere. As reference materials for XPS and NEXAFS measurements, powdered Na$_2$HPO$_3$ (P$^{3+}$), Na$_2$HPO$_4$ (P$^{5+}$) and DPA were also measured. These powdered samples were embedded in an indium plate.

The chemical states of the sample surfaces were determined by XPS using 3000 eV photons. The charging effect due to the electron emission was eliminated by using a flood gun. The binding energy was normalized by Al $1s$ of Al$_2$O$_3$ at 1561.2 eV [17].

NEXAFS spectra were taken by three different modes. The first is the total electron yield (TEY) mode. In this mode, the sample drain current was plotted as a function of the photon energy. The second is the partial electron yield (PEY) mode where the intensity of the low-energy electrons ($\sim E_K=50$ eV) detected with the electron energy analyzer was plotted. The third is the photoelectron yield (PY) mode. In this mode, the intensity of the specific photoelectrons was plotted as a function of the photon energy. We chose a suitable detection mode depending on the desired detection depth. The NEXAFS spectra were normalized by the photon flux, which was monitored by the current of aluminum foils in front of the sample.

For the NIXSW measurements, the sample surface was irradiated by X-rays from the surface normal. The method of NIXSW was in principle the same as the NEXAFS measurements. The PY mode was adopted for the NIXSW measurements. For the PY modes, the take-off direction of photoelectrons was 55 degree from the surface normal.

III. RESULTS AND DISCUSSIONS

First, we will show the chemical states of the sapphire surface and molecular configuration of SAM on the basis of the XPS and NEXAFS results. Figure 1 shows the XPS wide-scan for SAM excited by 3000 eV photons. Narrow scans in the P 1s and C 1s regions are shown in small insets together with those of the powdered DPA. The binding energies of P 1s and C 1s for SAM are almost the same as those for the powdered DPA, which suggests that the covalent bonds are not formed between sapphire and DPA molecules. It should be noted that the intensity ratio of the C 1s/P 1s for SAM is higher than that for powdered DPA. Since the powdered DPA molecules are randomly oriented, the high intensity of C 1s for SAM suggests that the alkyl chains of DPA molecules in SAM are located at the upper side, while the phosphonic acids in DPA molecules are located at the lower side.

Figure 2 shows the P 1s-NEXAFS spectra for SAM and powdered reference materials. For all spectra, the intense resonance peaks are observed at 2152.8 eV (marked B). For Na$_2$HPO$_3$, another peak is also observed at 2150.8 eV (marked A). For P K-edge NEXAFS spectra of PO$_4^{3-}$...
and PO_{4}^{5+}, Kuper et al. have calculated by MS Xo method using P_{4}O_{6} and P_{4}O_{10} clusters, respectively [18]. They assigned that the most intense resonances for P_{4}O_{6} and P_{4}O_{10} are the transitions from the P 1s to the 5e+5a_{1} and 6e orbitals, respectively. Compared with their calculations, we assign the lower-energy peak (marked A) observed in Na_{2}HPO_{4} to the P 1s→5e+5a_{1} resonance. The higher-energy peaks (marked B) observed in Na_{2}HPO_{4}, DPA and SAM are assigned to the P 1s→6e resonance. This resonance is also included in the NEXAFS for P_{4}O_{6} [18], so it is seen as a shoulder in the NEXAFS of Na_{2}HPO_{3}.

The phosphorus atom in a phosphoric acid (P^{5+}) is bonded to four oxygen atoms, while the phosphorus atom in a phosphonic acid (P^{3+}) is bonded to three oxygen atoms. The phosphorus atom in a DPA molecule is bonded to three oxygen atoms and one carbon atom in the alkyl chain. The NEXAF spectrum for powdered DPA suggests that the formal oxidation state of phosphorus atom in a DPA molecule is close to pentavalent state rather than trivalent state. The energy of the main peak for SAM is almost the same as that for phosphoric acid (P^{5+}). The result suggests that the phosphoric acid does not decompose and the phosphorus atom remain pentavalent state. If the covalent bond of P–O–Al is formed with the surface, the phosphorus atom is negatively charged compared with that in the P–O bond, because the aluminum atom has highly positive nature. But no chemical shift between powdered DPA and SAM was observed in P 1s XPS spectrum (Fig. 1). The results suggest that the phosphonic acid in the DPA molecule does not form the covalent bond with the surface, and the DPA molecules are adsorbed on the surface by electrostatic interaction forming ionic bonds.

In order to confirm the molecular configuration obtained by XPS, i.e., the alkyl chains of DPA molecules in SAM are located at the upper side while the phosphonic acids are located at the lower side, the geometrical locations of phosphorus and carbon atoms at the surface were precisely determined by NIXSW method. We will firstly check the applicability of the NIXSW method to the sapphire surface on the basis of the total electron yield. Figure 3 shows the total electron yield (TEY) as a function of the photon energy for clean surface of sapphire. Several peaks due to the standing wave from the sapphire substrate were observed in soft X-ray region (2000 eV - 4000 eV). The most intense peak is observed around 3050 eV, which is due to the standing wave originating from the sapphire substrate. This energy nearly corresponds to one of the Bragg diffraction peaks from α-Al_{2}O_{3} with corundum structure [19]. The wavelength of this energy is 0.41 nm, which corresponds to d = 0.21 nm. This length is nearly corresponding to the one-sixth of the C-axis of sapphire unit cell. The narrow scan around this peak is shown in the small inset. The TEY once decreases a little and suddenly increases. Such intensity modulation in TEY is characteristic to the single crystal surface at Bragg condition [4].

Now, we will check the validity of NIXSW method on the basis of the total electron yield. The NIXSW utilizes the spatial variation of electric field intensity of the standing wave generated by the coherent interference between incident X-rays and Bragg diffracted ones. The NIXSW method has been successfully applied to the determination of atomic-scale position of adsorbed atoms on metal surfaces [7-11], and the detailed processes of calculations were reviewed [20,21]. Here we will briefly show the methods for the calculation to determine the atomic position on oxide surface in line with the present case.

The normalized intensity of the photoelectron (I(E)/I_{0}) being concerned is described as

\[ I(E)/I_{0} = 1 + R(E) + 2F[R(E)]^{1/2} \cos[2\pi d_H - \delta(E)] \] (1)

where R(E) is the reflectivity of the substrate as a function of the photon energy, \( \delta(E) \) is the energy-dependent phase modulation caused by the X-ray standing wave, F is the structure factor, and \( d_H \) is the coherent position of the atoms measured from the surface [12]. The photon energy, E, is normalized by the “W parameter” that stands

![FIG. 2. Phosphorus K-edge NEXAFS spectra for SAM of DPA on sapphire and various phosphate compounds.](http://www.sssj.org/ejsnt)
FIG. 4. Total electron yield for clean sapphire substrate around 3050 eV as a function of photon energy. The incidence angle of X-rays was surface normal. Also displayed are the theoretical curves calculated by the equation (1) for four different coherent positions assuming that the atoms being concerned are located at \( d_H \) from the surface.

FIG. 5. \( \text{P} 1s \) photoelectron yield for SAM on sapphire around 3050 eV as a function of photon energy. The incidence angle of X-rays was surface normal. Also displayed are the theoretical curves calculated by the equation (1) for four different coherent positions assuming that the phosphorus atoms are located at \( d_H \) from the surface.

FIG. 6. \( \text{C} 1s \) photoelectron yield for SAM on sapphire around 3050 eV as a function of photon energy. The incidence angle of X-rays was surface normal. Also displayed are the theoretical curves calculated by the equation (1) for four different coherent positions assuming that the carbon atoms are located at \( d_H \) from the surface.

In order to confirm the validity of the calculation, we firstly plot the normalized intensity of the total electron yield as a function of the photon energy. The result is shown in Fig. 4. Also displayed are the theoretical curves calculated by the equation (1) for four different coherent positions assuming that the atoms being concerned are located at \( d_H \) from the surface. The data apparently follow the curve for \( d_H = 0 \) (or \( d_H = 1 \)). In this case, the total electron yield is mostly originating from the \( \text{Al} 1s \) photoelectrons. Thus it is natural that the aluminum atoms in the surface region are located just at the coherent position. So it was confirmed that the methods can be applied to the determination of the atomic position of the atoms on the surface.

Figures 5 and 6 show the intensities of the \( \text{P} 1s \) and \( \text{C} 1s \) photoelectrons, respectively, as functions of the photon energy together with the theoretical curves. The intensity of the \( \text{P} 1s \) apparently follows the theoretical curve for \( d_H = 0.5 \). This means the phosphorus atoms in DPA molecules are located at the half of the coherent position. The coherent position corresponds to the 0.21 nm, which is deduced from the Bragg energy. So it is obtained that the phosphorus atoms are located at 0.11 nm from the surface.

As to the more detailed configuration of phosphonic acid on the surface, we consider as follows. A phosphorus atom in a DPA molecule is bonded to three oxygen atoms and one carbon atom with nearly tetrahedral structure. The XPS results show that the DPA molecule is bonded to surface through phosphonic acid while the alkyl chain is located at upper side. So, two stable configurations are considered. In the first case, the phosphorous atom is bonded to the surface through \( \text{P}–\text{O}–\text{Al} \) bond that is perpendicular to the surface. Considering that the lengths of the \( \text{P}–\text{O} \) and \( \text{P}=\text{O} \) (or \( \text{Al}–\text{O} \)) bonds are in the order of 0.15 nm, the phosphorus atoms should be located at about 0.3 nm from the surface, which is fairly larger than the result obtained by the NIXSW. In the second case, the phosphorus atom is bonded to the surface through three equivalent \( \text{P}–\text{O} \) bonds with tetrahedral configuration. In this case, the distance between the phosphorus atom and the surface is estimated to be about 0.1 nm, if we assume that the \( \text{P}–\text{O}–\text{Al} \) bond length is 0.3 nm. This value is almost same as the result obtained by the NIXSW. Thus it is shown that the three oxygen atoms in a phosphonic acid are equivalently located at the lower side, while the \( \text{P}–\text{C} \) bond points to the upper side.

On the other hand, Fig. 6 shows that the intensity of the \( \text{C} 1s \) photoelectron does not follow the theoretical curve, and there is no intensity modulation. This means that the alkyl chain is not parallel to the surface, and there is no exact position of carbon atoms.

In conclusion, the NIXSW results support the former speculation that the phosphonic acids in DPA are located at the lower side, while the alkyl chain is located at the upper side. This means that the DPA molecules form
clear SAM on a sapphire surface through the phosphonic acid. This is the first study for the structure determination of adsorbed molecules on an oxide surface by the NIXSW method. The present results shed light on the further applications of NIXSW method to the structure analysis of atoms and molecules on insulating materials like oxides.

IV. SUMMARY

We have investigated the surface structure of decylphosphonic acid (DPA, C\(_{10}\)-alkyl phosphonic acid) adsorbed on a sapphire surface by NIXSW as well as XPS and NEXAFS. We observed clear profiles of the photoelectron intensity around 3050 eV due to the standing wave from the sapphire substrate. Compared with the simulation using the crystal parameters, it was found that the phosphorus atoms are located at 0.11 nm from the surface, while the constant height was not observed for carbon atoms. The results are consistent with the observations by XPS and NEXAFS measurements where the molecules form SAM on sapphire surface through the phosphonic acid, while the alkyl chain is located at the upper side. Also it is suggested that the phosphorus atom is bonded to the surface through three oxygen atoms while the P-C bond points to the upper side. The present results shed light on the further applications of NIXSW method to the structure analysis of atoms and molecules on insulating materials like oxides.

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