Immobilization of Alkyl Chain Molecules on Oxide Surface Using Phosphonic Acid as an Anchor*

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For the purpose of formation of stable and uniform organic films on oxide surface, the alkyl chain molecules were immobilized on oxide surfaces using phosphoric acid as an anchor. The molecule investigated was decyl-phosphonic acid (DPA), which is composed of C₁₀-alkane chain and one of the ends is terminated by phosphonic acid (PO₃H₂). DPA films are formed on sapphire surfaces by solution methods; immersing the substrate in DPA ethanol solution. The chemical-states of the interface between DPA molecules and the sapphire were investigated by X-ray photoelectron spectroscopy (XPS) and near-edge X-ray absorption fine structure (NEXAFS) using synchrotron soft X-rays. As to the P *K*-edge NEXAFS spectra of the DPA film on the sapphire C-plane, the resonance energy of the main peak was the same as that of the molecular DPA. This result indicates that the DPA molecules keep the molecular state. XPS spectra measured under total reflection condition shows that the phosphonic acid group in DPA molecules is located at the lower side, while the alkyl chain is oriented at the upper side on the surface. In order to confirm the thermal stability of the DPA film, the film was heated at 250°C. The peak intensity of the P *K*-edge NEXAFS spectra decreased, while the intensities of P 1s and C 1s in XPS spectra increased by heating. This discrepancy was explained by the difference of the detection depths between NEXAFS and XPS. Based on the simulation using a simple model, it was found that the DPA molecules form island structures at room temperature, while they become the uniform film after heating. As a result, it was concluded that the uniform and thermally stable films of alkyl chain molecules was formed on the sapphire surface, and phosphonic acid is an excellent anchor that combines alkyl molecules on oxide surface. [DOI: 10.1380/ejssnt.2012.367]

Keywords: X-ray photoelectron spectroscopy; Near edge extended X-ray absorption fine structure (NEXAFS); Aluminum oxide; Phosphorus

I. INTRODUCTION

Organic thin films are expected for new device materials to the next generation, because they have a lot of advantages such as high flexibility, eco-friendly nature, and transparency. In order to apply organic thin films to device materials, it is necessary to form uniform organic thin films on inorganic substrates such as metals and oxides. However, it is difficult to immobilize organic molecules on the surface of an inorganic material and to form stable and uniform films because of the lattice mismatch between organic crystals and inorganic solids.

Recently, the method to immobilize molecules and form stable films on metal substrates was established. The films formed by this method are called self-assembled monolayer (SAM). For this method, thiol groups are used as an anchor to immobilize organic molecules on noble metal surfaces [1, 2], because sulfur atoms form strong chemical bond with noble metals. Some studies have been reported for the formation of organic SAMs on metal sur-

faces such as gold [3, 4], silver [5] and copper [6, 7].

On the other hand, formation of SAMs on oxide surfaces had not been realized, although oxides are important as device substrate materials because of their useful properties such as transparency and diversity of electric conductivity from wide-gap insulator to metal. Up to now, several methods have been tried to form uniform organic thin films on oxides. Silvezan *et al.* reported the formation of the organic films on silica surfaces using silanation reaction through trichlorosilane groups [8]. Also Sagiv *et al.* tried to form organic monolayer on a glass using silicon alkoxide [9]. For the thermally stable organic thin films on oxides, Gao *et al.* investigated structure change of alkylphosphonate films on zirconia at various temperatures by nuclear magnetic resonance (NMR), and elucidated that the film is stable up to 50°C [10]. In our previous study, we reported the formation of stable alkyl chain molecules on a sapphire surface using silicon alkoxide as an anchor [11]. We also clarified that oxygen atoms in the silicon alkoxide groups form covalent bonds with aluminum atoms in the sapphire, and the molecules are oriented on the surface [11].

However, the formation of stable SAMs on oxide surface at higher temperature has not yet been realized. In order to establish the most suitable condition of the SAM formation, it is necessary to investigate the chemical states

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of the interface between the organic molecules and oxide surfaces.

As functional groups that combine organic molecules with oxides, phosphoric acid is known to be one of the candidate groups. It is known that phosphoric acid groups have a strong affinity for oxides. So they are often used as coating materials for oxides [12]. Also, the phosphoric acid is used for non-photocatalyst in the form of phosphated titania [13], because the phosphoric acid is easily incorporated in titanium oxides.

In this study, we present the formation of the thermally stable films of alkyl chain molecules using phosphonic acid as an anchor on oxide surfaces. The system investigated was the decyl-phosphonic acid (DPA) molecules adsorbed on sapphire surfaces. This molecule is composed of C10-alkane chain and one of the ends is terminated by phosphonic acid (PO_3H_2). The chemical states of the interface between DPA molecules and the oxide surface and thermal stability of the film were investigated by X-ray photoelectron spectroscopy (XPS) and near-edge X-ray absorption fine structure (NEXAFS) using soft X-rays from synchrotron light source.

II. EXPERIMENTAL

The experiments were performed at the BL27A station of Photon Factory in the High Energy Accelerator Research Organization (KEK-PF). The X-rays were emitted from the bending magnet. The InSb(111) double crystals were used as a monochromator. The energy of X-rays covered from 1.8 keV to 4.2 keV. The energy resolution ($\Delta E/E$) was 5×10^{-4} .

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

For the heating experiment, the infrared YAG laser ($\lambda = 1.06 \mu\text{m}$) was used, and the laser beam was directly irradiated on the surface from the outside of the vacuum chamber through the optical fiber. Surface temperatures were measured by a pyrometer.

Polished R-plane (1 $\bar{1}$ 02) and C-plane (0001) of sapphire (Jiazuo City Crystal Photoelectric Materials Co., Ltd.) were used as substrates. The surface of sapphire was rinsed by supersonic waves in ethanol for 15 min. Decyl-phosphonic-acid (DPA, $\text{CH}_3-(\text{CH}_2)_9-\text{PO}(\text{OH})_2$, Tokyo Chemical Industry Co., Ltd.) was used as adsorbed molecules. This molecule is composed of C₁₀-alkane chain, and one of the ends is terminated by phosphonic acid (PO_3H_2). For comparison, Na_2HPO_4 (P^{+5}), Na_2HPO_3 (P^{+3}) and Na_2HPO_2 (P^{+1}) were used as standard materials.

Thin film samples were prepared by solution methods. The sapphire substrate was immersed in 0.01 Mol/dm³ DPA ethanol solution for 20 h. After immersing, the substrate was rinsed by supersonic waves in ethanol for 15 min and dried. For comparison, a powdered DPA sample was also measured. This sample was prepared by embedding the DPA powder in the surface of an indium plate.

The surface chemical states were measured by X-ray photoelectron spectroscopy (XPS). The binding energy

FIG. 1: P *K*-edge NEXAFS spectra for (a) reference materials and powdered DPA, and (b) the DPA film on sapphire C-plane.

was normalized by O 1s of Al_2O_3 at 531.6 eV [14]. The ionization cross sections (σ) of P 1s and C 1s excited by 3000 eV are 5.24×10^4 barns and 1.70×10^3 barns, respectively. So the intensities were normalized by the ionization cross sections. The incident angle of X-rays for normal XPS measurements was 35° , and the takeoff direction of photoelectrons was surface normal. Also we measured XPS at 0.5° incidence. The critical angle of X-ray total reflection at 3 keV is 0.8° [15], so the X-rays are totally reflected at 0.5° incidence.

NEXAFS spectra were taken by the total electron yield (TEY), monitoring the sample drain current. The NEXAFS spectra were normalized by the photon flux, which was monitored by the current of aluminum foils in front of the sample.

III. RESULTS AND DISCUSSION

Figure 1 shows P *K*-edge NEXAFS spectra of phosphoric acid compounds, the powdered DPA sample and the DPA film sample on the sapphire C-plane surface. The two resonance peaks were observed. For the spectra of Na_2HPO_2 and Na_2HPO_3 samples, the peaks appeared at low energy side (marked A) are the resonance from P 1s to $5e+8a_1$ orbitals in PO_3^{3-} , and the peaks appeared at high energy side (marked B) are that from P 1s to 6e orbitals in PO_4^{3-} [16]. The energy of the main peak for the DPA film sample is the same as that for the powdered DPA. This result indicates that the DPA molecules do not decompose and keep the molecular state. Also the energy of the main peak for DPA film is almost the same as that for

FIG. 2: (a) Relation between thickness of DPA and XPS peak intensity ratio of $I_{P\ 1s}/I_{Al\ 1s}$ at 3000 eV calculated by Eq. (1). (b) Wide-scan XPS spectrum of the DPA film on sapphire C-plane excited by 3000 eV photons. Narrow scans in the C 1s and P 1s regions are shown in small insets.

TABLE I: Binding energies of P 1s and C 1s, the peak intensity ratios of $I_{P\ 1s}/I_{Al\ 1s}$, and thickness d (nm). The value of $I_{P\ 1s}/I_{Al\ 1s}$ was normalized by the photoionization cross sections [17]. The thickness d was obtained from the plot of Fig. 2(a).

	B. E. (eV)		$I_{P\ 1s}/I_{Al\ 1s}$	d (nm)
	P 1s	C 1s		
Powdered DPA	2149.7	284.6	—	—
DPA on sapphire C-plane	2149.9	284.9	0.024	3.1
DPA on sapphire R-plane	2150.4	285.5	0.057	8.1

Na₂HPO₄ sample. The formal oxidation numbers of the phosphorus atoms are monovalent (P⁺¹) for Na₂HPO₂, trivalent (P⁺³) for Na₂HPO₃ and pentavalent (P⁺⁵) for Na₂HPO₄, respectively. These results indicate that the phosphorus atoms in the DPA film keep the pentavalent state on the surface.

Next, we estimate the thickness of the DPA film using the peak intensities of P 1s and Al 1s obtained from XPS spectra. Figure 2(b) shows the wide scan XPS spectra of the DPA film on the sapphire C-plane. The narrow scans of C 1s and P 1s are also shown in small insets. The intensity ratio of the photoelectrons, $I_{P\ 1s}/I_{Al\ 1s}$, is expressed as

$$\frac{I_{P\ 1s}}{I_{Al\ 1s}} = \frac{\sigma_{P\ 1s} \cdot \lambda_{P\ 1s\ \text{in DPA}} \cdot n_{P\ 1s\ \text{in DPA}} \cdot \{1 - \exp(-d/\lambda_{P\ 1s\ \text{in DPA}})\}}{\sigma_{Al\ 1s} \cdot \lambda_{Al\ 1s\ \text{in Al}_2\text{O}_3} \cdot n_{Al\ \text{in Al}_2\text{O}_3} \cdot \exp(-d/\lambda_{Al\ 1s\ \text{in DPA}})}, \quad (1)$$

where σ is the photoionization cross section [17] for the respective photoelectron indicated as a subscript, λ is the inelastic mean free path (IMFP) of the photoelectrons in the material indicated as a subscript [18], n is the atomic concentration of an element in the material shown as a subscript, and d is the thickness of the layer in nm. In Fig. 2(a), the $I_{P\ 1s}/I_{Al\ 1s}$ ratio is plotted as a function of d (nm). Using the experimental values of $I_{P\ 1s}/I_{Al\ 1s}$, thickness d was obtained from Fig. 2(a). The thickness of the DPA films on sapphire C-plane and R-plane was 3.1 nm and 8.1 nm, respectively. The results are shown in Table I. Concerning the crystal plane indices, the value of sapphire R-planes are larger than that of sapphire C-planes. So it is considered that the DPA molecules are easy to adsorb on the surface of sapphire R-planes compared with that of C-planes. Thus, the DPA film on the sapphire C-plane is near to the monolayer compared with that on the R-plane. So in the following discussion, we will concentrate on the results for the film on the sapphire C-plane.

Figure 3 shows the C 1s and P 1s XPS spectra at two incident angles for the DPA film on the sapphire C-plane. The photoelectron intensities of P 1s and C 1s were nor-

malized by that of Al 1s originated from the substrate. Moreover, in order to show clearly the difference of the C 1s intensities, the intensities of the P 1s was fixed the same. For the C 1s spectra, the intensity for $\theta = 0.5^\circ$ (total reflection condition) is enhanced compared with that for $\theta = 35^\circ$, while the intensities of P 1s peaks for two incident angles are almost same. Quantitatively, the value of $I_{C\ 1s}/I_{P\ 1s}$ obtained for $\theta = 0.5^\circ$ was 0.17, while the value of that obtained for $\theta = 35^\circ$ was 0.093. The XPS measured at $\theta = 0.5^\circ$ is surface sensitive method, because the incident X-rays are totally reflected on the surface [19]. Namely, these results mean that the carbon atoms are dominant on the topmost surface. As a result, it indicates that the alkyl chain of the DPA molecules is located at the upper side, while the phosphonic acid is the lower side on the surface. The result is in consistent with that obtained by normal incidence X-ray standing wave methods for the same system [20].

Next, we shall explain the chemical-states of the interface between the DPA films and the sapphire surface. From the results of Fig. 3, we clarified that the carbon atoms in alkyl chains are oriented at the upper side, and the phosphorus atom is located at lower side on the sur-

FIG. 3: C 1s and P 1s XPS spectra excited by 3000 eV photons at two incident angles for DPA film on sapphire C-plane. Intensities of C 1s and P 1s were normalized by that of Al 1s.

FIG. 4: P 1s XPS spectra excited by 3000 eV photons for powdered DPA and DPA film on sapphire C-plane.

face. Thus, for the discussion about the chemical-states of the interface, we will concentrate on the P 1s XPS spectra. The results are shown in Fig. 4. Although it is expected that the phosphonic acid in DPA interacts with the sapphire surface, the difference of the binding energy is not observed in Fig. 4. Considering the electronegativities of

TABLE II: Intensity of resonance peak (**R**) in NEXAFS spectra obtained from $(I - I_0)/I_0$, where I_0 is the normalized TEY at the off resonance energy and I is that at the resonance peak energy (see Fig. 5), and the XPS peak intensity ratio (**r**) of $I_{P\ 1s}/I_{Al\ 1s}$. The $I_{P\ 1s}/I_{Al\ 1s}$ was normalized by the photoionization cross sections [17]. The subscripts 1 and 2 indicate before and after heating at 250°C.

		Before heating	After heating	After/Before
$\frac{I - I_0}{I_0}$	(R)	3.8×10^{-3} (R ₁)	1.8×10^{-3} (R ₂)	$\frac{\mathbf{R}_2}{\mathbf{R}_1} = 0.47$
$\frac{I_{P\ 1s}}{I_{Al\ 1s}}$	(r)	0.024 (r ₁)	0.058 (r ₂)	$\frac{\mathbf{r}_2}{\mathbf{r}_1} = 2.4$

oxygen and phosphorus atoms, the oxygen atom is more negatively charged than the phosphorus atom in the P–O bond of the DPA molecules. Assuming that 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. So the peak energy of the P 1s must shift to the lower binding energy side. Actually, for the formation of the alkyl chain films on the sapphire surface through silicon alkoxide, we have elucidated that the covalent bonds of Si–O–Al are formed on a sapphire surface, and the Si 1s peak for the film shifts to higher binding energy side by 1.4 eV than that for the molecular silicon alkoxide [11]. In the present case, however, no chemical shift is observed in the P 1s peaks between the powdered DPA and the film. It indicates 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.

Figure 5 shows the P *K*-edge NEXAFS spectra and the C 1s and P 1s XPS spectra before and after heating at

FIG. 5: Left: P K -edge NEXAFS spectra for DPA films on sapphire C-plane before and after heating. I_0 is the normalized TEY at the off resonance energy and I is the normalized TEY at the resonance peak energy. Right: C $1s$ and P $1s$ XPS spectra excited by 3000 eV photons for DPA film on sapphire C-plane before and after heating.

250°C by YAG laser. For the NEXAFS spectra, the intensity of the main peak decreased after heating. Here, in order to estimate the quantity of the DPA molecules on the surface, the peak intensity was expressed as $(I - I_0)/I_0$ where I_0 is the normalized TEY at the off resonance energy ($h\nu = 2148.0$ eV) and I is the normalized TEY at the resonance peak energy ($h\nu = 2152.7$ eV). The values of $(I - I_0)/I_0$, which is indicated as $\mathbf{R}$, are shown in the first line of Table II. The value of $\mathbf{R}$ before heating is 3.8×10^{-3} , and that after heating is 1.8×10^{-3} . So the value of $\mathbf{R}$ after heating decreased to 0.47 compared with that before heating.

For NEXAFS measurement, the sample drain current was measured which corresponds to total electrons emitted from the surface. The kinetic energies of the electrons emitted from the surface are mostly lower than 10 eV, because the photoelectrons and Auger electrons lose the kinetic energy by inelastic scattering. The inelastic mean free path (IMFP) of these low energy electrons ($E_K < 10$ eV) is longer than 10 nm [20]. From the results of Fig. 2, the thickness of the DPA on sapphire C-plane was 3.1 nm. This value is fairly smaller than the IMFP of low energy electrons. Therefore, the value of $(I - I_0)/I_0$ is proportional to the quantity of adsorbed DPA molecules on the surface. So the result means that the quantity of the DPA molecules decreased to 0.47 by thermal desorption during the heating.

On the other hand, for the P $1s$ and the C $1s$ XPS spectra, the photoelectron intensities after heating increased compared with the respective peak intensities before heating. In appearance, these results are inconsistent with the NEXAFS results.

We shall explain the reason for this discrepancy. For XPS measurement, the photoelectrons excited by 3000 eV photons were detected. The kinetic energy of the P

$1s$ photoelectrons is about 850 eV, and the IMFP is 1.7 nm [21]. This value is fairly small compared with the detection depth of NEXAFS. Thus, XPS is more surface sensitive than NEXAFS in the present case. Namely, the increase in photoelectron intensities by heating suggests that the DPA molecules before surface heating formed island structures, while DPA molecules diffused and became uniform film by heating.

In order to confirm this consideration, we calculated the ratio of the thickness of the DPA film before and after heating using schematic models shown in Fig. 6. In these models, we assume that the adsorbed molecules form the n -pieces (m -pieces) of islands with same shape. The intensity of the resonance peak ($\mathbf{R}$) observed in the NEXAFS spectra is defined as

$$\mathbf{R} = \frac{I - I_0}{I_0}. \quad (2)$$

Using this value, the intensity ratio of the resonance peaks before and after surface heating, $\mathbf{R}_1/\mathbf{R}_2$, is expressed as

$$\frac{\mathbf{R}_2}{\mathbf{R}_1} = \frac{Y \cdot d_2}{X \cdot d_1}, \quad (3)$$

where X and Y are the sum of the area of DPA islands before and after heating, respectively, d_1 and d_2 are the average thickness of the DPA film before and after heating, respectively. The ratio of the P $1s$ photoelectron intensity before and after heating, $\mathbf{r}_1/\mathbf{r}_2$ is expressed as

$$\frac{\mathbf{r}_2}{\mathbf{r}_1} = \frac{Y \cdot d}{X \cdot d'}, \quad (4)$$

where d is the detection depth of the P $1s$ photoelectron. From Eqs. (3) and (4), the value of $(\mathbf{R}_2/\mathbf{R}_1)/(\mathbf{r}_2/\mathbf{r}_1)$ is

FIG. 6: Schematic model of DPA films before (a), and after (b) heating at 250°C. In this model, we assume that the adsorbed molecules form n -pieces (m -pieces) of islands with same shape. x is average area of an island, and X is the sum of the areas of total islands before heating. y is average area of an island, and Y is the sum of the areas of total islands after heating. d_1 and d_2 are the average thickness of the DPA film before and after heating, respectively. d is detection depth of P 1s photoelectrons.

given as follows

$$\frac{\mathbf{R}_2/\mathbf{R}_1}{\mathbf{r}_2/\mathbf{r}_1} = \frac{d_2}{d_1}. \quad (5)$$

The values of $\mathbf{R}_2/\mathbf{R}_1$ and $\mathbf{r}_2/\mathbf{r}_1$ are listed in the third column of Table. II. As a result, we obtained the value of d_2/d_1 is 0.20. This value indicates that the average thickness of the film became 1/5 by the surface heating compared with that before heating. As mentioned above, the thickness of the film on the sapphire C-plane was 3.1 nm. It is considered that the DPA film after heating became uniform layers.

Concerning the chemical states of the interface between the phosphonic acid in the DPA molecule and the sapphire surface, it was elucidated from Fig. 4 that the DPA molecules are adsorbed on the surface by electrostatic interaction. Considering the result that the DPA film was stable up to 250°C, it is suggested that the phosphonic acids in DPA molecules are bonded with the surface not through Wan-der-Waals force, but likely through ionic bonds.

In conclusion, we succeeded in forming thin films of alkyl chain molecules on sapphire surfaces through phosphonic acid as an anchor by solution methods. The film became thermally stable and uniform by heating. For the structure of the film, it was supposed that the phosphonic acids in DPA molecules are located at the lower side on the surface. As a result, we propose that the phosphonic acid is an excellent anchor to immobilize and form the organic film on oxide surfaces. Since the alkyl chain of the DPA molecule is oriented upper side on the surface, the

film of DPA molecules might become an excellent mold to connect organic functional molecules on oxides if the reverse side of the phosphonic acid in the alkyl chain is modified by functional groups.

IV. SUMMARY

We have investigated the formation of the thermally stable films of alkyl chain molecules on sapphire surface using phosphoric acid as an anchor. For the chemical-states of the DPA molecules on the surface, it was elucidated that the DPA molecules keep molecular state. As to the molecular configuration, the phosphonic acid in the DPA molecule is located at lower side, while the alkyl chain is oriented upper side on the surface. Relating to the thermal stability of the DPA films, it was clarified that the DPA film on the sapphire surface became uniform after heating. As a result, we succeeded in forming uniform and thermally stable films of alkyl chain molecules on the oxide surfaces using phosphonic acid as an anchor.

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