Immobilization of alkyl chain molecules with phosphonic acid on oxide surface

Ayumi NARITA*1,2, Yuji BABA1, Tetsuhiro SEKIGUCHI1, Iwao SHIMOYAMA1, Norie HIRAO1, Tsuyoshi YAITA1,2
1Quantum Beam Science Directorate, Japan Atomic Energy Agency,
Tokai-mura, Naka-gun, Ibaraki 319-1195, Japan
2Graduate School of Science and Engineering, Ibaraki Univ., Mito-shi, Ibaraki 310-8512, Japan

1 Introduction
In order to apply organic thin films as optical or electronic device materials, it is important to form uniform and stable films on solid surfaces. However, the immobilization of organic molecules on oxide surfaces is difficult because oxides are chemically inert. Phosphoric acid is one of functional groups which have high affinity for oxides. In this study, we have investigated the immobilization of alkyl chain molecules on the oxide surface through phosphonic acid as an anchor.

2 Experiment
All experiments were performed at the BL-27A station, C(0001) face of sapphire plates were used as substrates. We chose decylphosphonic acid (DPA) molecules as an adsorbate. The DPA film was formed by immersing the substrate in 0.01 Mol/dm³ of DPA ethanol solution, and the substrate was rinsed by supersonic waves in ethanol. The chemical states of the interface were measured by X-ray photoelectron spectroscopy (XPS) and near-edge X-ray fine structure (NEXAFS). The sample was heated up to 250°C in vacuum by YAG laser from the outside of the vacuum.

3 Results and Discussion
The XPS spectra were measured at two incident angles; one was 35° and the other was 0.5° (total reflection condition). The C 1s peak intensity for the total reflection condition is enhanced compared with that for 35°. The XPS measured for the total reflection condition is surface sensitive, so the results suggest that the carbon atoms are located at the topmost surface. 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.

Fig. 1 shows P K-edge NEXAFS and P 1s XPS spectra of the DPA film before and after heating. For the NEXAFS spectra, the main peak at 2152.8 eV is the resonance from P 1s to unoccupied orbital localized at the P atom [1]. The intensity of the peak decreased after heating. The detection depth of the NEXAFS measured by total electron yield is deeper than 10 nm, so the peak intensity is proportional to the total amount of the DPA molecules. Therefore, the NEXAFS results indicate that a part of DPA molecules were desorbed from the surface.

For the XPS spectra, on the other hand, the peak intensity of photoelectrons increased after heating. The P 1s photoelectron was excited by 3000 eV photons, so the kinetic energy of the P 1s photoelectrons is 850 eV. The inelastic mean free path (IMFP) of P 1s photoelectrons is 1.7 nm [2]. Therefore, it is suggested that the DPA molecules forming island structures at room temperature changed to thin uniform layer by heating. Thus, the increase of the photoelectron intensity of the P 1s in spite of the decrease of the DPA molecule quantity indicates that the surface was homogeneously covered by DPA molecules and the film became uniform by heating.

In summary, we succeeded in forming uniform and thermally stable films of alkyl chain molecules on the oxide surfaces using phosphonic acid as an anchor.

References

* narita.ayumi@jaea.go.jp

Fig.1 Left : P K-edge NEXAFS spectra for DPA films on sapphire C-plane before and after heating. I₀ is the normalized TEY at the off resonance energy and I is the normalized TEY at the resonance peak energy. Right : P 1s XPS spectra excited by 3000 eV photons for DPA film on sapphire C-plane before and after heating. The Intensity was normalized by that of Al 1s originated from substrates.