Self-assembled Multilayer Formed by Alternate Stacking of Zirconium and Terephthalic Acid Layers

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A self-assembled multilayer consisting of transition metal and biscarboxyl acid was fabricated by simply immersing an oxide-covered silicon substrate into zirconium (Zr) *n*-butoxide and terephthalic acid (TPA) solutions alternately. In this multilayer, two TPA monolayers were bridged with a Zr^{IV} monolayer. The chemistry connecting these monolayers is most likely coordinate bonds between Zr^{IV} ions and carboxyl groups.

Organic films, spontaneously organized at a solid substrate surface during the chemisorption process, drastically alter the physical and chemical properties of the substrate.[1] Although such "self-assembly" is a powerful means to fabricate organic monolayers similar to the Langmuir–Blodgett (LB) method, it has difficulty in fabricating multilayers. In order to fabricate multilayers on oxide substrates, a "self-assembly" method based on silane coupling chemistry is first reported.[2] This method was not simple but complicated somewhat, since it required the protection and activation processes of organosilane molecules when self-assembling them and before stacking a upper layer, respectively. Mallouk and co-workers developed a promising method in which monolayers of alkyl-bisphosphonic acid and zirconium (Zr) ions were alternately stacked.[3] Their method has proved to be quite useful to fabricate a variety of functional multilayers.[4–12] Carboxylic acid is promising as an alternative to phosphonic acid, since aliphatic acid moleclues were reported to be immobilized on a Zr^{IV}-modified oxide surface,[13] due to fairly strong coordinate bonds between Zr^{IV} ions and carboxyl groups; however, self-assembled multilayers composed of a metal–carboxylic acid complex have not been fabricated so far. Here, we show that coordination chemistry between Zr and caroboxylic acid is applicable to fabricate self-assembled multilayers.

Silicon (Si) substrates were cleaned by a photochemical method.[14] A thin oxide layer less than 2-nm thick was grown on the cleaned substrates. Consequently, the substrate surfaces became hydrophilic so as to be most certainly terminated with hydroxy groups. These substrates were first immersed in a Zr compound solution (zirconium(IV) *n*-butoxide solution, 80 wt % in 1-butanol, purchased form Sigma-Aldrich Co. and used as received) for 10 min. This immersion process was conducted at room temperature in a glove box in which humidity was regulated to about 15%RH. The substrate were rinsed with 1-butanol, sonicated in 1-butanol for 10 min and then dried with nitrogen gas flow. This series of the surface treating procedures is referred to as the Zr-process. Next, the substrates were immersed in a 3 mM solution of terephthalic acid (TPA, 98%, Sigma-Aldrich Co.) in *N*,*N*-dimethylformamide (DMF, 99.5%, Nacalai Tesque, Inc.). The immersion was prolonged for 30 min in the atmosphere. The substrates were sonicated in DMF for 10 min and then blown dry. This series of the procedures is referred to as the TPA-process. The Zr-process and TPA-process were repeated appropriately.

The thickness of the layers grown on each substrate was measured using a spectroscopic ellipsometer (FE-5000, Otsuka Electronics Co.) as summarized in Figure 1. Thickness increased almost linearly with the number of surface modification processes. It increased about 0.6 nm with one Zr-process and TPA-process set. This value is accounted for by considering that Zr and TPA monolayers are stacked through the corresponding processes. It is noteworthy that thickness increased throughout Zr-process, while it rarely increased through TPA-process. This reason is discussed below.

Figure 2 shows X-ray photoelectron spectra (XPS, measured using an XPS system, Kratos Analytical Ltd., ESCA3400) of a sample surface which has been treated through 6 pairs of Zr-process and TPA-process. The XPS Zr 3d profile as shown in Figure 2a consists of two peaks corresponding to Zr $3d_{3/2}$ and Zr $3d_{5/2}$. These peaks are centered at 183.3 and 185.7 eV, respectively, clearly demonstrating the incorpration of Zr^{IV} ions into the film.[15] The XPS C 1s profile as shown in Figure 2b consists of two main peaks centered at around 284 and 290 eV corresponding to carbon atoms in aromatic rings and carboxyl groups, respectively. As shown in Figure 2c, the XPS O 1s profile consists of one main peak centered at 533 eV with a sub peak at 532 eV. The former is a signal from the SiO_2 layer under the grown film, while the latter corresponds to oxygen atoms in carboxyl groups interacted with Zr^{IV} ions. As demonstrated in Figure 2d, this carboxylic O 1s component of the 3-layer, that is, Zr–TPA–Zr, sample is small so that it is observed as a right tail of the main peak of SiO_2.

The growth behavior of a TPA–Zr self-assembled multilayer is depicted as shown in Figure 3. First, zirconium(IV) *n*-butoxide molecules chemisorb on a hydroxylated oxide surface similarly to zirconium(IV) *t*-butoxide molecules.[13] Two of the alkoxy groups are believed to remain on the surface as illustrated in

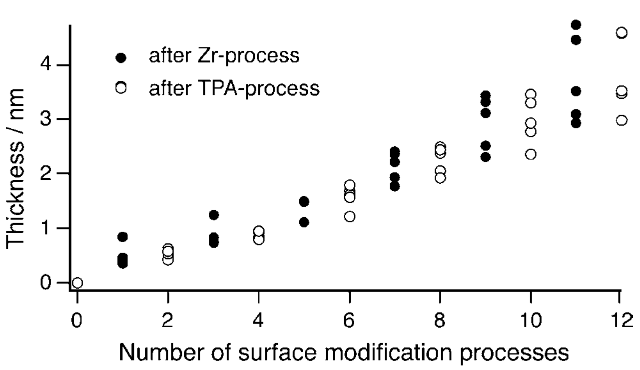

Figure 1. Thicknesses of layers grown on oxide-covered Si substrates by alternately conducted Zr-process and TPA-process.

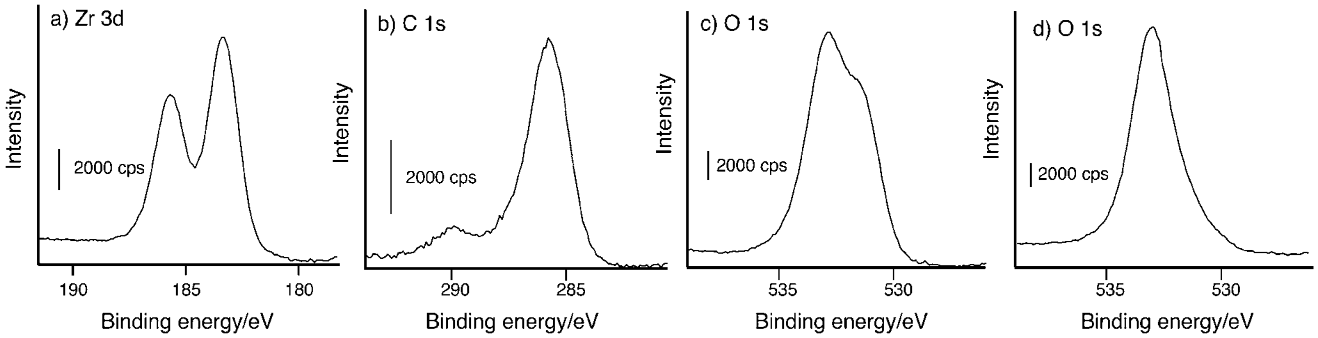

Figure 2. XPS peak profiles of the samples treated by the Zr- and TPA-processes. a) Zr 3d, b) C 1s, c) O 1s spectra of the Zr(6 layers)–TPA(6 layers) sample, and d) O 1s spectrum of the Zr–TPA–Zr sample.

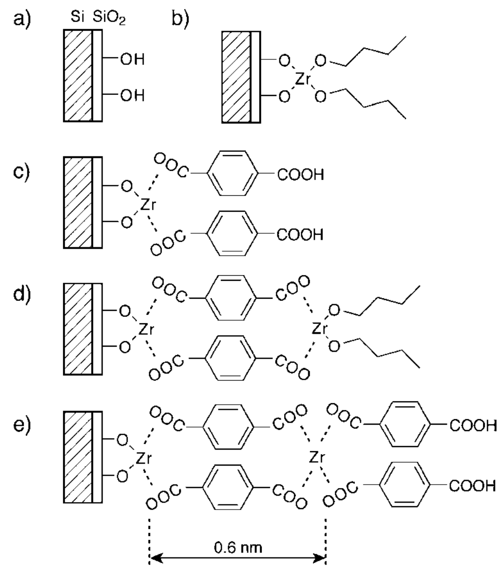

Figure 3. Schematic illustration of the growth behavior of Zr–TPA self-assembled multilayer. a) A Si substrate with hydroxylated surface oxide, b) termination of the surface oxide of the Si substrate with zirconium(IV) *n*-butoxide, c) immobilization of TPA molecules on the Zr^{IV}-modified substrate surface, d) modification of the carboxylated surface with a Zr^{IV} layer, and e) further stacking a TPA monolayer.

Figure 3a. Such a surface terminated with alkoxide molecules is reported to strongly interact with aliphatic acids such as alkyl carboxylic and phosphonic acids. Consequently, acid molecules are self-assembled on the Zr-modified surface to form a monolayer firmly adhered to the surface.[13,16] Coordination chemistry of Zr ions where carboxyl or phosphonic groups serve as ligands has been considered as a driving force to promote the chemisorption of organic acids. Therefore, when the sample surface modified with zirconium *n*-butoxide is treated by TPA-process, TPA molecules similarly chemisorb onto the surface, resulting in the formation of a self-assembled monolayer terminated with carboxyl groups as depicted in Figure 3c. Since the remaining butoxy groups on the surface are thought to be removed due to hydrolysis and then replaced with TPA molecules, the layer thickness is almost unchanged between the Zr-modified and the subsequent TPA-chemisorbed states. This assumption agrees with the results shown in Figure 1. On the carboxyl-terminated surface, zirconium(IV) *n*-butoxide molecules are able to be chemisorbed again (Figure 3d) by the second Zr-process. On this Zr-modified surface, one more self-assembled monolayer is formed by the second TPA-process (Figure 3e). By repeating the Zr-process and TPA-process, a self-assembled multilayer is formed consisting of TPA monolayers bridged by Zr monolayers.

In conclusion, we have succeeded in fabricating a self-assembled multilayer consisting of aromatic biscarboxylate, i.e., TPA, monolayers, and transition metal, i.e., Zr^{IV}, monolayers by means of the layer-by-layer chemisorption method. Our method is promising since a wide variety of organic biscarboxyl molecules are applicable in order to design novel functions.

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