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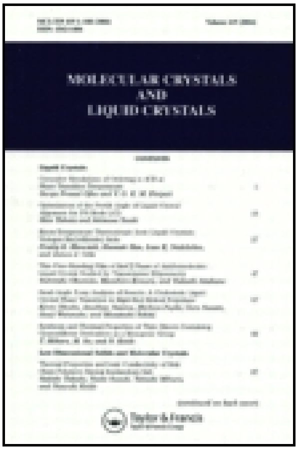

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In-situ AFM Observation of the Formation Process of Layer-by-Layer Sequential Adsorption Film

Takeshi Yamada [a] & Seimei Shiratori [a]

[a] Departmant of Applied Physics & Physico-informatics, KEIO Univ, 3-14-1 Hiyoshi, Kouhoku-ku, Yokohama, Kanagawa, 223-8522, Japan

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In-situ AFM Observation of the Formation Process of Layer-by-Layer Sequential Adsorption Film

TAKESHI YAMADA and SEIMEI SHIRATORI

Departmant of Applied Physics & Physico-informatics, KEIO Univ., 3-14-1 Hiyoshi, Kouhoku-ku, Yokohama, Kanagawa, 223-8522, Japan

Recently, layer-by-layer sequential adsorption technique is applied to many devices. We reported that the thickness and the surface structure of the layer-by-layer sequential adsorption film using Poly (allylamine hydrochloride) (PAH) and Poly (acrylic acid) (PAA) were systematically controlled with nm scale order by changing pH of polyelectrolytes solution. In this study, we present the first observation results on the initial adsorption processes of polyelectrolytes to the substrate in solution by in-situ observation using an AFM. It was found that the surface structure was strongly effected by the previously formed under layer and the solution pH.

INTRODUCTION

Recently, layer-by-layer sequential adsorption technique, started by Decher[1], becomes one of the important method to fabricate ultra-thin film. It is applied to many devices, such as organic EL devices and sensors. This technique needs positively and negatively charged polyelectrolytes solution. The first step is to dip a charged substrate into oppositely charged polyelectrolytes solution. The second step is to dip into the other polyelectrolytes solution. By continuing this process, layer-by-layer sequentially adsorbed film has alternate layers of negatively and positively charged polyelectrolytes. FIGURE 1 is simple model of this method. We can control the film thickness and surface structure by changing solution pH[2][3]. However, the adsorption process of polyelectrolytes was not obvious.

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In this study, we observed the formation process of layer-by-layer sequentially adsorbed polyelectrolytes film by using in-situ atomic force microscopy (AFM) observation in water solution for the first time.

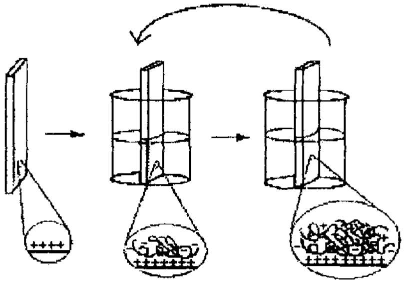

FIGURE 1 Model of layer-by-layer sequentially adsorption technique

EXPERIMENTAL SECTION

We used Poly (allylamine hydrochloride) (PAH, Mw=70,000, Aldrich chemical company, Inc.) and Poly (acrylic acid) (PAA, Mw=90,000, Polyscience, Inc.). The density of each solution of polyelectrolyte was 10^{-2}M. And to adjusted solution pH, HCl and NaOH were added. For in-situ observations, we used an AFM (Shimadzu SPM model SPM-9500J2), a laboratory dish type solution vessel and a Si_3N_4 cantilever (k=0.12N/m). The observation was carried out in contact mode. We used SiO_2 substrate.

RESULTS AND DISCUSSIONS

PAH and PAA solution were adjusted to pH 3.5 by HCl. PAH solution of pH 3.5 was injected into the AFM vessel and in-situ observation was started. FIGURE 2 shows PAH layer surface onto SiO_2 substrate after 30 minutes. PAH formed thin and smooth layer.

After this step, the vessel was rinsed by pure water well, and pH 3.5 PAA solution was injected. FIGURE 3 shows PAA layer surface onto previously formed PAH layer after 30 minutes. The PAA layer was formed thin and smooth layer, too.

Then the vessel was rinsed and pH 3.5 PAH solution was injected. As soon as PAH solution was injected, PAH was adsorbed onto surface.

FIGURE 4 shows this surface after 16 minutes. The PAH layer was formed nucleus of PAH and it was grow up. The generation was saturated after 15 min.

FIGURE 5 shows the surface image of the film after the adsorption of 10 bilayers. The nucleuses of polyelectrolytes were gathered onto the surface. During the sequential adsorption process, new nucleuses of polyelectrolytes were adsorbed and covered surface.

The adsorption form of polyelectrolytes was dependent on the surface

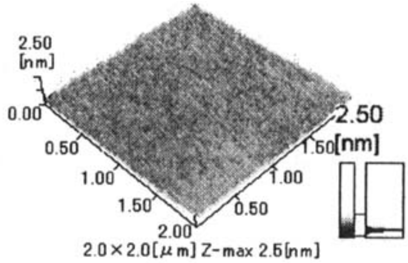

FIGURE 2 AFM image of PAH layer surface (1st layer)

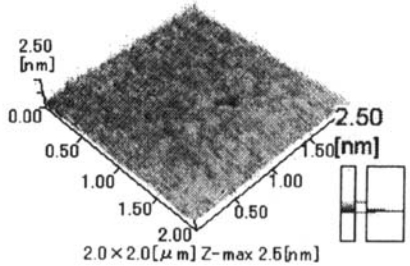

FIGURE 3 AFM image of PAA layer surface (2nd layer)

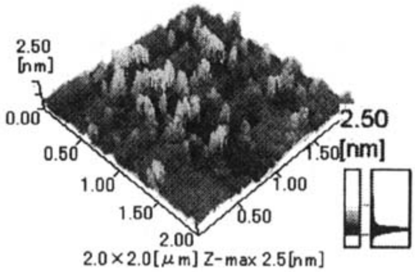

FIGURE 4 AFM image of PAH layer surface (3rd layer)

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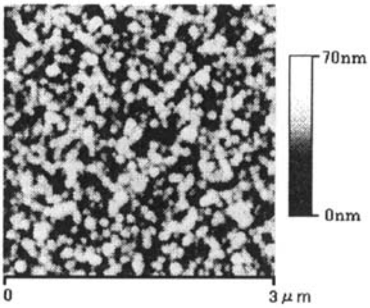

FIRURE 5 AFM image of $(PAH/PAA)_{10}$ adsorbed film surface

structure of previously adsorbed layer. The first bilayer was formed thin and smooth layers. After the first bilayer, grain state polyelectrolytes were adsorbed and covered the surface. The surface structure of layer-by-layer sequentially adsorbed polyelectrolytes film was formed at the adsorption process from solution.

CONCLUSION

We have succeeded the in-situ observation of the sequential adsorption process of PAH and PAA by using AFM. The adsorption form was dependent on the solution pH and the surface structure of previously adsorbed layer. It was found that surface microstructure was not formed after the drying process but formed during the adsorption process in the solution.

Acknowledgments

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