Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Ultra-Thin Organic/Inorganic Hetero-Structures for Photonic Crystal by Mass-Controlled Layer-by-Layer Sequential Adsorption Method

Seimei Shiratori [a] & Takahiro Ito [a]

[a] Keio University, Department of Applied Physics & Physico-informatics, Hiyohsi, Kouhoku-ku, Yokohama, 223-8522, Japan

Version of record first published: 24 Sep 2006

To cite this article: Seimei Shiratori & Takahiro Ito (2001): Ultra-Thin Organic/Inorganic Hetero-Structures for Photonic Crystal by Mass-Controlled Layer-by-Layer Sequential Adsorption Method, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 371:1, 143-146

To link to this article: http://dx.doi.org/10.1080/10587250108024708

Mol. Cryst. and Liq. Cryst., 2001, Vol. 371, pp. 143-146

Ultra-Thin Organic/Inorganic Hetero-Structures for Photonic Crystal by Mass-Controlled Layer-by-Layer Sequential Adsorption Method

SEIMEI SHIRATORI and TAKAHIRO ITO

Keio University, Department of Applied Physics & Physico-informatics, Hiyohsi, Kouhoku-ku, Yokohama, 223-8522, Japan

By the combination of surface sol-gel process of metal alkoxides (TiO_2) and the mass-controlled layer-by-layer sequential adsorption process of polyelectrolytes, highly ordered organic / inorganic interface was successfully fabricated. The one dimensional photonic crystal such as photorefractive device can be produced by using this method owing to the large differences of the refractive index between the layers.

Keywords layer-by-layer; sequential adsorption; polyelectrolyte; sol-gel; mass-control; photonic crystal; TiO_2

INTRODUCTION

Layer-by-layer sequential adsorption process of polyelectrolytes[1] makes it possible to fabricate thin organic films simply through the sequential dipping of a substrate into dilute polycation and polyanion solutions [2]. This technique is a promising film fabrication process because high performance devices such as EL devices[3], smoke sensors[4] and air cleaning filters[5] have been produced using this process. However, this has been applied only for polyelectrolytes. If this process can be extended not only to polymers but to inorganic materials, the variety of the materials used for this process will be greatly enlarged. In this study, by the combination of surface sol-gel process of metal alkoxides[6] and the mass-controlled layer-by-layer sequential

adsorption process of polyelectrolytes, organic/inorganic hetero structure thin film was successfully fabricated. We present the new method for constructing organic/inorganic hetero structure thin film for photonic crystals[7] by using the mass-controlled automatic dipping system with a quartz crystal microbalance (QCM) thickness monitor for layer-by-layer sequential adsorption process [8].

EXPERIMENTAL

The schematic figure for the automatic dipping system for the deposition of TiO_2/ polyelectrolyte thin film is shown in Fig.1[3,6]. The adsorption of materials was controlled and measured by the QCM feedback control system.

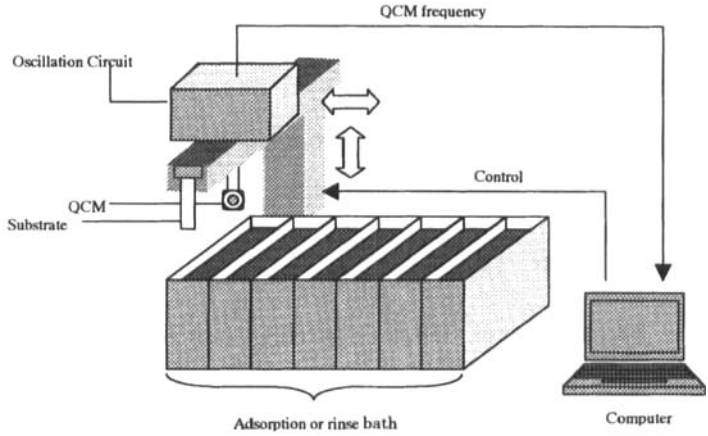

Figure1 Automatic dipping system for mass-controlled layer-by-layer film.

Titanium butoxide was used as adsorption material and 100mM solution was made to solve metal alkoxide in ethanol/toluene. Two repeated blocks of (polymer/ TiO_2 gel) thin film were deposited on polystyrene substrate with QCM thickness monitor. They were immersed in titanium butoxide in toluene/ethalol, rinsed in ethanol, hydrolyzed in pure water, immersed in

ethanol, and dried. This process was repeated 50 cycles. On the other hand, the organic layer was deposited by the sequential adsorption film of poly(allylaminnehydrochloride) (PAH) and poly(acrylic acid)(PAA) .

RESULTS & DISCUSSIONS

Fig.2.(A) and 2(B) were frequency shift of QCM and the observation of cross sectional TEM image, when ((TiO_2) gel film) / (organic polyelectrolyte film) hetero structure was deposited onto QCM and polystyrene substrate. As shown in this figure, highly ordered organic/inorganic hetero structure was easily fabricated by wet process. Polyelectrolyte was adsorbed to non-organic layer because of existing hydrolytic group hydrolyzed from botoxylic group. From Fig.2(A), the frequency shift of the thickness monitor of the first and the third block were found to be 4000 and 3800 Hz, respectively. The values corresponds to the measured thickness observed from Fig.2(B): the first and the third block from the substrate of the polyelectrolytes film thickness was approximately 110nm and 90nm, respectively. On the other hand, from Fig.2(A), it was found that the frequency shifts of the second and the forth block were 2900 and 3400 Hz. The values corresponds to the measured thickness observed from Fig.2(B):the second and the forth block of the TiO_2 layers were approximately 68nm and 72nm, respectively. By the estimation from these values, the incremental thickness of the frequency shift of the QCM thickness monitor was found to be approximately 0.02nm/Hz.

From the measurement using ellipsometry, the values of refractive index were found to be 1.40 for the polyelectrolytes film and 1.89 for TiO_2 film. By utilizing the large differences between the layers, we consider that one dimensional photonic crystal [8] for optical devices can be produced by this method.

CONCLUSIONS

Both of the mass increase in the adsorption of the titanium butoxide layer and the polyelectrolytes layers showed linear relationship as the increase of the dipping cycles. The linear growth of the film thickness and the highly organized hetero structures of polymer/TiO_2 film was observed by QCM and TEM. The new wet process is considered to be promising for the fabrication of photo refractive devices using one dimensional photonic crystals.

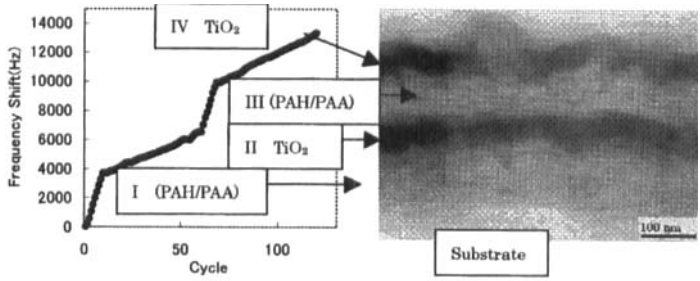

Figure2. (A)Frequency shift of QCM for $[(PAH/PAA)_{10}+(TiO_2)_{50}]_2$ heterostructure. (B) Cross sectional TEM image of $[(PAH/PAA)_{10}+(TiO_2)_{50}]_2$ heterostructure.

Acknowledgements

A part of this work was supported by TEPCO research foundation and Kurata Science Foundation 1999-2000. The automatic dipping system for the thin film was fabricated by Nippon Laser Electric Lab. We thank Dr. Izumi Ichinose of RIKEN , prof.M.F.Rubner and Dr. K.Wada of Massachusetts Institute of Technology for the discussion and advise on this study.

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