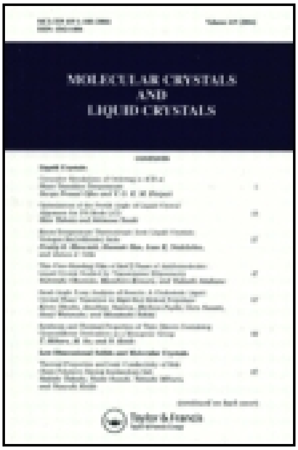

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PREPARATION OF VERTICALLY HETEROSTRUCTURAL MULTILAYER MICROPATTERNS USING PATTERNED MULTILAYER TEMPLATES

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PREPARATION OF VERTICALLY HETEROSTRUCTURAL MULTILAYER MICROPATTERNS USING PATTERNED MULTILAYER TEMPLATES

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A new approach to realize multilayer micropatterns with vertical heterostructure is introduced. In this approach, well-defined micropatterns of poly(4-vinylpryridine) (PVP) and poly(acrylic acid) (PAA) multilayer are prepared in short process time by using microfluidic channels combined with the convective self-assembly process (i.e., the self-assembling process in the presence of external flow). The resulting patterns were then used as templates for further spin-coating process of poly(diallyldimethyl ammonium chloride) (PDAC) and poly(sodium 4-styrenesulfonate) (PSS). The micropatterns with sharp edge boundaries and small ridges at the edges were obtained for alternating $(PVP/PAA)_5/(PDAC/PSS)_{40}$ *multilayers.*

Keywords: convective self-assembly; microfluidic channel; template; vertical heterostructure

INTRODUCTION

Multilayer thin films have widely been investigated for the applications to thin film devices based on electrochemical processes such as sensors, integrated optics, rectifiers, or light-emitting devices (LED) [1,2]. To fabricate high performance devices with organic or organic/inorganic hybrid multilayer thin films, the internal structure of the films should be well organized on the degree of high molecular order and the ability to pattern with at least micrometer-scale feature on the films is also required.

Recently, several methods for multilayer patterning have been reported including selective deposition of polyions onto the template made by microcontact printing and electric field-directed deposition [3–5]. In these methods, the adsorption process is based on self-diffusion and

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rearrangement due to the interactions between adsorbing molecules and templates. As a result, alternating regions with chemically different functionality should be introduced on the substrate to achieve the selective deposition.

We have previously demonstrated the convective self-assembly (SA) in microfluidic channels as an effort to produce well-defined micropatterns of multilayer thin films in short process time [6,7]. In present study, we extend the convective SA to the fabrication of multilayer micropatterns with vertical heterostructure.

EXPERIMENTS

Gold substrates were prepared by sputtering of titanium of 100 Å thickness as an adhesion-promoting layer, followed by 1000 Å of gold, onto silicon wafers (Si/SiO_2) (Namkang Hi-Tech). Poly(4-vinylpyridine) (PVP, $M_w = 60{,}000$), poly(acrylic acid) (PAA, $M_v \sim 450{,}000$), poly(diallyldimethyl ammonium chloride) (PDAC, $M_w = 100{,}000 \sim 200{,}000$), and poly(sodium 4-styrenesulfonate) (PSS, $M_w = 70{,}000$) were purchased from Aldrich and used without further purification. All the polymer solutions were 10 mM (repeat unit basis) in N, N-dimethylformamide (DMF) or ethanol for PVP and PAA, and Milli-Q water for PDAC and PSS, respectively. Substrates with COOH-terminated self-assembled monolayers (SAM) were prepared by immersing the gold-coated silicon wafer into a 5 mM 16-mercapto-hexadecanoic acid (Aldrich) in absolute ethanol for 30 min.

For the patterning of multilayer thin films with vertical heterostructure, we employed the convective SA in two steps. *(1) Preparation of templates by convective SA in microfluidic channels*: The microfluidic channels were formed by the contact between an elastomeric poly(-dimethylsiloxane) (PDMS) mold and a hydrophilic substrate [7,8]. The PDMS stamp was prepared from a silicon master with patterns realized by conventional photolithography. First, the microfluidic channels were filled with a polymer solution by the capillary pressure, which allowed the polymer chains to absorb onto the substrate. The residual polymer solution was then removed by the spinning process. The filling process of polymer solution was completed within 3 s and the spinning process was carried out at 6000 rpm for 2 min. These two processes were repeated 5 times for the PVP/PAA bilayer. *(2) Spin SA on patterned multilayer template*: After the micropatterns of $(PVP/PAA)_5$ multilayer films on a substrate were obtained, the PDMS stamp was removed and alternate deposition of PDAC and PSS onto the micropatterns was carried out by the spin SA as follows: a few drops of polyelectrolyte solution were placed onto the patterned multilayer template and the substrate was then rotated at 4000 rpm for

20 s. After the deposition of each polyelectrolyte layer, the substrates were thoroughly rinsed with a plenty of deionized water. The spinning time and speed for the washing step were identical to those for the layer deposition.

The formation of multilayer thin films was monitored by UV-Vis spectrometer and the feature of patterns was observed by atomic force microscopy (AFM, Nanoscope IIIa) and optical microscopy (OM).

RESULTS AND DISCUSSION

Figure 1 shows the UV-vis absorption spectra for the multilayer films of PDAC/PSS and PVP/PAA with different number of bilayers, respectively. Positively charged PDAC and negatively charged PSS were alternately spin self-assembled through the electrostatic attraction. This alternate deposition of individual polyelectrolyte is verified by the linear increase in absorption band at 227 nm, originating from the adsorbed PSS chains. The absorption band at 256 nm is also assigned to the contribution of the adsorbed PVP chains and also increases linearly with increasing number of bilayers. This implies that the (PVP/PAA) multilayer based on the hydrogen bonding was uniformly self-assembled by spin coating.

A patterned multilayer template of PVP and PAA was obtained by the convective self-assembly in microfluidic channels. To prepare the microfluidic channels, a PDMS mold was placed on a silicon wafer covered with a COOH-terminated self-assembled monolayer. The dimension of each channel is 10 μm in width, 1.2 μm in height, and 5 mm in length. Figure 2

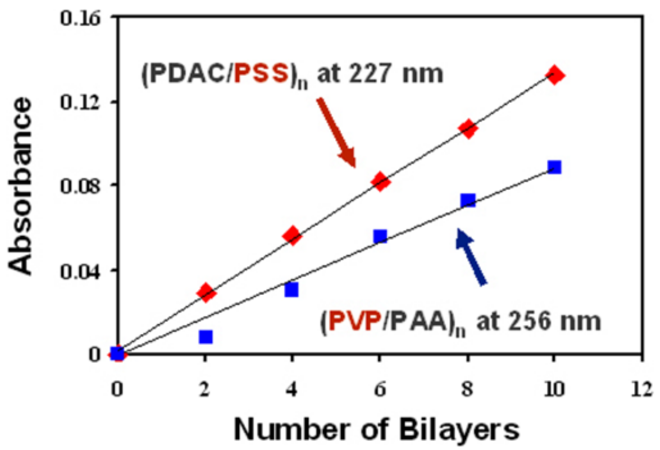

FIGURE 1 UV-Vis spectra of (a) $(PDAC/PSS)_n$ and (b) $(PVP/PAA)_n$ multilayer films with different number of bilayers. (See COLOR PLATE V)

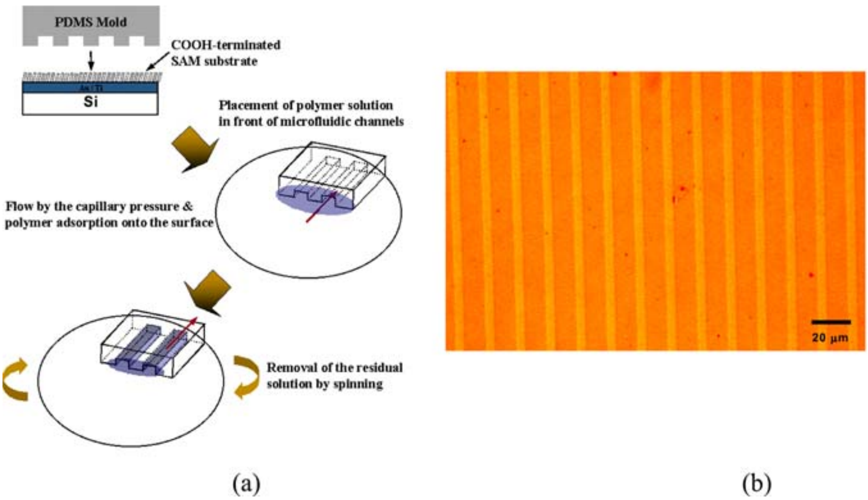

FIGURE 2 (a) Schematic of convective self-assembly in microfluidic channels and (b) OM image of patterned $(PVP/PAA)_5$ multilayer film. (See COLOR PLATE VI)

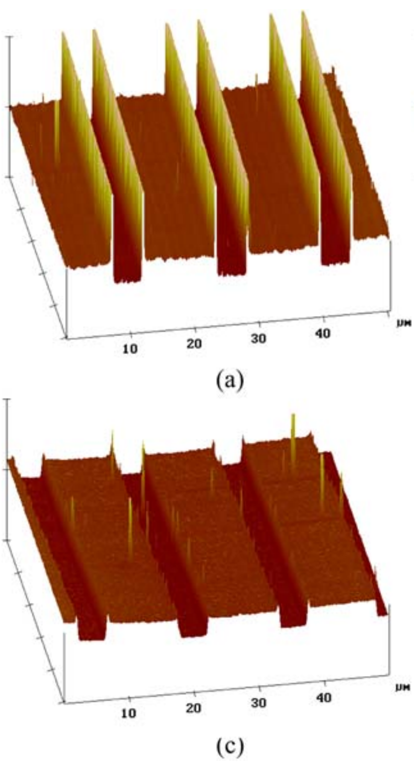

FIGURE 3 AFM images of patterned multilayer of $(PVP/PAA)_5$ when the solvent is (a) ethanol, (b) ethanol/H_2O (90/10), and (c) DMF (Z scale is 50 nm/div). (See COLOR PLATE VII)

represents a schematic for the fabrication of patterned multilayer films and an OM image of a $(PVP/PAA)_5$ film formed.

It is noted that the shape of patterned $(PVP/PAA)_5$ multilayer template is significantly dependent on the wettability of solvent on PDMS wall. As shown in Figure 3, micropatterns with sharp edge boundary and small ridge at the edge were obtained by using DMF as a solvent. When ethanol was used as a solvent, high ridge or wall was developed at the edge of patterned lines due to the preferential wetting of ethanol on the PDMS walls, and such a high ridge (or wall) was remarkably diminished by mixing ethanol with water.

The alternate deposition of PDAC and PSS was carried out by the spin SA on the patterned $(PVP/PAA)_5$ multilayer template, which was prepared by using DMF as a solvent. Carboxylic acid groups of PAA, the top layer of the template, are partially ionized and thus enable the adsorption of cationic PDAC polyelectrolytes. The AFM topography images of 4, 8, 20, and 40 bilayers consisting of PDAC and PSS bilayers are shown in Figure 4.

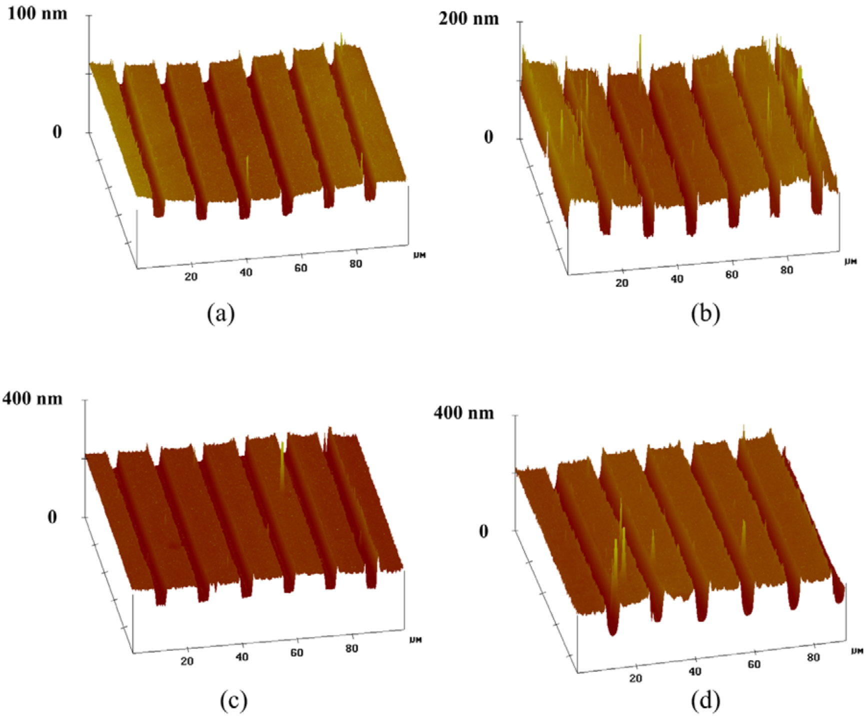

FIGURE 4 AFM images of patterned multilayer of $(PVP/PAA)_5$ $(PDAC/PSS)_n$: (a) $n=4$, (b) $n=8$, (c) $n=20$, (d) $n=40$. (See COLOR PLATE VIII)

The feature heights are 24, 30, 57, and 86 nm, respectively. These multilayer micropatterns with vertical heterostructure have high line resolution and small ridge at the edge boundary. The surface of the micropatterns with heterogeneous vertical structure is also quite homogeneous and smooth.

CONCLUSIONS

A new approach to realize multilayer micropatterns with micron-size feature and vertical heterostructure has been described. Well-defined micropatterns of $(PVP/PAA)_5$ multilayer were first prepared by the convective SA with microfluidic channels and then used as a template for the additional spin SA of PDAC and PSS. The vertically heterostructural multilayer micropatterns with high line resolution and small ridge at the edge boundary were produced.

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