

Build-up of Multilayered Thin Lines using Sequential Adsorption of Polymers in Microfluidic Channels

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ABSTRACT

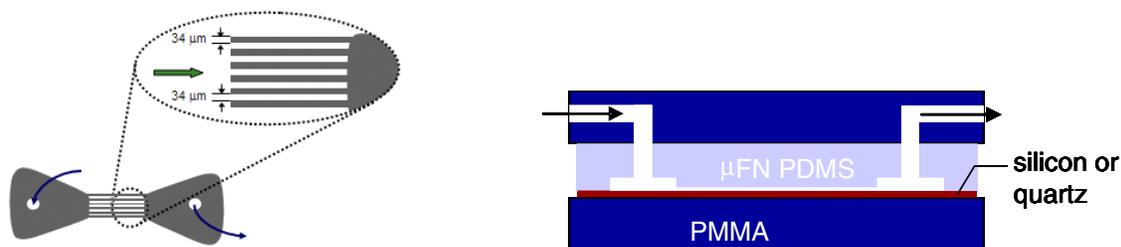
There is a constant desire towards the improvement of both the processing and design of new micro-patterned circuits to be used in modern technologies, but numerous routes are available to achieve such improvements. We are pursuing new methods to create multilayers self-assembled thin films with high spatial resolution. Our research is based on the coupling of two well-known techniques: Layer-by-Layer (LbL) Assembly and flow in Microfluidic Networks (μ FNs), the latter guiding the multilayer deposition to occur within microchannels. Here, we report on preliminary results regarding the achievement of polymeric multilayer assemblies of poly(sodium-4-styrenesulfonate) and poly(allylamine hydrochloride) with well-defined patterns. Using AFM, we show that steady-state layer-by-layer deposition of our polymers occurs when the solutions are made to flow sequentially through the μ FN. The results suggest future capabilities to design assembled structures with control over chain conformation and, eventually, an ability to control the orientation and thickness of the polymeric multilayers.

INTRODUCTION

One of the first reports related to the build-up of polymeric multilayered coatings was due to Decher and coworkers [1] and interest in such polymeric thin coatings has grown progressively due to anticipated diverse applications. Layer-by-layer (LbL) assembly consists of the sequential exposure of a substrate to alternating polyanion and polycation solutions to allow build-up of highly interpenetrated multilayers with fine thickness resolution of 2-5 nm per bilayer pair. While LbL assembly is a viable approach for the growth of spatially homogeneous multilayers, a complementary process exists for the processing of micron-sized structures wherein a thermosetting liquid is cured within the microchannels of a silicone stamp. This process, known as MIMIC (MicroMolding In Capillaries), is a key element to our present investigation. Char et al. [2] applied the MIMIC process to sequential polyelectrolyte adsorption, though without the continuous flow applied in the present study. In our work, we have used pressure driven flow of polyelectrolyte solutions through a μ FN made with soft lithography [3]. This process, termed microfluidic polyelectrolyte assembly (μ PA) allows micron-resolved multilayer growth on silicon, quartz, or even thermoplastic films. Importantly, we utilize only a compression seal of the PDMS stamp to the substrate, using a simple manifold, so that the resulting surface structures can be easily characterized by disassembling the device. Here, we investigated the role of salt added to the polyelectrolyte solutions in determining the LbL growth behavior as determined using AFM.

EXPERIMENTAL

The deposition of polyelectrolytes by microfluidic polyelectrolyte assembly (μ PA) was performed on silicon (100) substrates. Silicon substrates were treated with piranha solution (70:30 $\text{H}_2\text{SO}_4/\text{H}_2\text{O}_2$) at 80 °C for 1 h, followed by rinsing in ultra-pure water (Milli-Q, $\rho > 18 \text{ M}\Omega\cdot\text{cm}$). To facilitate the adsorption of the first polymeric layer and to have a positively charged surface, we spin-coated a low molecular weight poly(ethyleneimine) (PEI) solution at 3000 rpm for 8 sec, followed by washing with water. The polyanion



Scheme 1. Schematic of the microfluidic device: (left) network structure and (right) manifold design. used in our experiments was poly(sodium-4-styrenesulfonate) (PSS), $M_w=70$ kDa, and $pK_a \sim 7$. The polycation was poly(allylamine hydrochloride) (PAH), $M_w=15$ kDa and $pK_a \sim 8.5$. The polymer deposition was done from aqueous solutions with polymer concentration 10^{-2} M and $pH=3.5$. At this pH, both the PSS [4] and PAH [5] are fully ionized. The effect of salt concentration on the layer thickness was studied using NaCl concentrations of 0.05 and 0.1 M. The elastomeric microfluidic network (μ FN) was fabricated from poly(dimethylsiloxane) (PDMS, Sylgard 184, Dow Corning) using a procedure described for making stamps used in microcontact printing. [3]

Our pattern consists of an array of 20 parallel lines, each 12 μ m thick, 34 μ m wide, 2.32 mm long, and separated by 34 μ m. The lines are connected to triangular reservoirs (5×10 mm²) at each end (Scheme 1, left). Delivery of solutions to and from this network is achieved with standard fittings connected to a PlexiglasTM manifold (Scheme 1, right) with ports located in line with holes punched through the stamp's thickness to the reservoir region. A seal is achieved by applying force between the top and bottom manifold plates. μ PA proceeds by first flowing the anionic PSS solution over the primed surface through the microfluidic network, flushing with ultra-pure water, then flowing the cationic PAH solution. This sequence is repeated multiple times. A flow rate of $2.167 \cdot 10^{-11}$ m³/s is used with a duration achieving three full flushes per solution, or 90 minutes per solution. Contact mode AFM images of dry multilayered patterns were obtained using a Topometrix TMX 2000 Scanning Probe Microscope.

RESULTS AND DISCUSSION

To obtain structural information about the multilayer films such as roughness and thickness, AFM measurements were performed on multilayers from μ PA processing on silicon wafers (Figure 1). We observe excellent replication of mold features in the polyelectrolyte patterns on the substrates. Thus, one can obtain multilayered lines by such a μ PA process as described. Thicknesses of the multilayers were obtained by differencing the darker (substrate + PEI) and lighter (multilayered stack) regions. This procedure is illustrated in Figure 1. For instance, after 6 bilayers of the μ PA process, the features obtained ($C=10^{-2}$ M, $pH=3.5$, $C_{NaCl}=0.1$ M) are around 15 nm high for a growth rate of approximately 2.5 nm/cycle (Figure 1). Additionally, the multilayered coatings are surprisingly smooth (RMS Roughness = 3.27 nm). Figure 2 shows the dependence of the layer thickness, measured with AFM, on the number of deposition cycles for different salt concentrations. We observe a linear dependence of the layer thickness on the deposition cycle number for each salt concentration, but with a large slope for higher salt concentration.

It is well established for quiescent LbL processing that ionic strength has strong effect on the structure of polyelectrolytes and the resulting LbL growth rate. In particular, the layers deposited at higher ionic strength are thicker, less interpenetrating, yielding less stable structures.[6] At low salt concentration, polyelectrolytes take on chain-extended conformations and adsorb as two dimensional chains, resulting in thin bilayer thicknesses of 13 Å for 0.05 M. At moderate salt concentration, the polymer chain takes on a more random coil or globular shape, leading to thicker layers (for 0.1 M NaCl, bilayer thickness of 25 Å). Our results on the effect of added salt, shown in Figure 2, are consistent with this picture, suggesting that for the flow rates employed the underlying mechanism of LbL adsorption is unmodified.

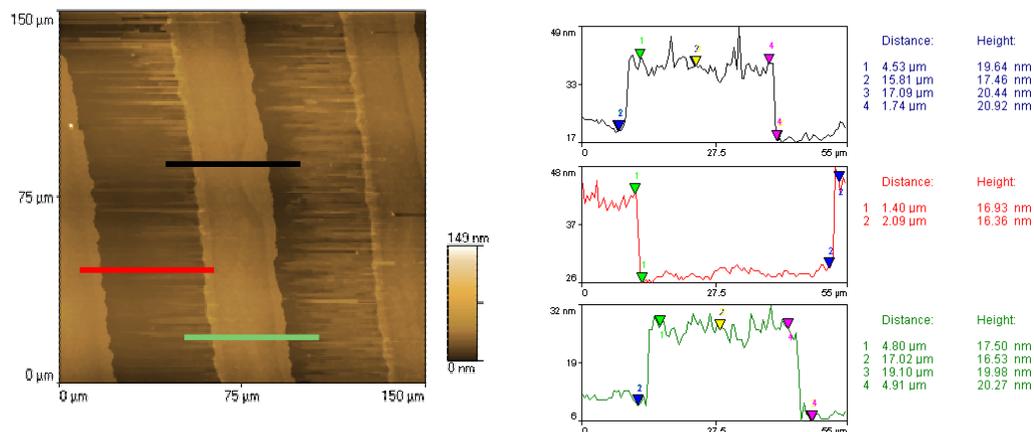


Figure 1. AFM 2D topographic of the microlines formed of 6 bilayer films of PSS/PAH (10^{-2} M, pH=3.5, $C_{\text{NaCl}}=0.1$ M) and line profile deposited by μ PA technique.

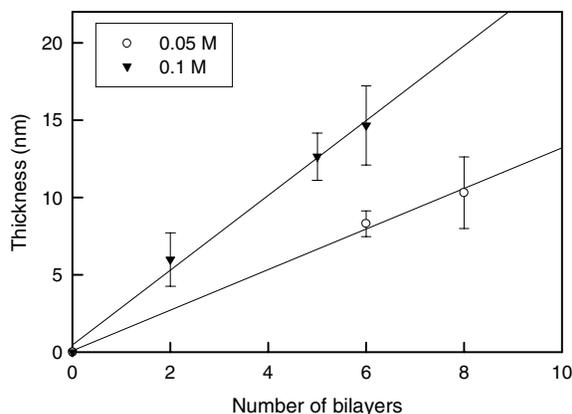


Figure 2. Features thickness from AFM vs. number of cycles for different salt concentration: 0.05 M (○) and 0.1 M (▼) of PSS/PAH films.

CONCLUSIONS

We have demonstrated the feasibility to pattern polyelectrolyte multilayers using flow of minimal quantities of polyelectrolyte solutions through tailor-designed microfluidic networks. It was found that we can control the bilayer growth rate of the μ PA process by the addition of salt. In the future, we plan to study the impact of varying flow rate on the growth rate and coating morphology and to determine the minimum feature size possible with available pressure driven flow equipment.

ACKNOWLEDGEMENTS

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