NANOSCALE PATTERNING OF POLYELECTROLYTE MULTILAYERS WITH WET STAMPING:

C. Cho(*) and N. S. Zacharia(*, ±)

(*) Materials Science and Engineering Program
Texas A&M University, College Station, Texas 77843

(±) Department of Mechanical Engineering
Texas A&M University, College Station, Texas 77843

Presented at the 15th International Coating Science and Technology Symposium,
September 13-15, 2010, St. Paul, MN[1]

Polyelectrolyte multilayers (PEMs) are one type of thin film potentially interesting for different applications and coatings such as ion transport, self-cleaning surfaces, drug delivery, and biomedical applications. They are fabricated by the layer-by-layer (LbL) method. This process results in a film deposition that can be controlled to the nanoscale. Electrostatic interactions are most commonly used, essentially creating a hydrogel that is bound together with ionic crosslinks, but other complementary interactions such as hydrogen bonding, metal ion/ligand interactions, or even covalent bonding can be used to form films. Spatial control over a soft surface's (such as an LbL film) physical and chemical properties is crucial for a number of these applications. Not just surface chemistry, but topographical and mechanical properties such as the degree of swelling and stiffness of the surface are also important. Different patterning techniques have been developed to acheive this such as photolithography, various microfluidic methods, microcontact printing, and nanoimprint lithography. There are a number of reports in the literature on the patterning of PEMs using the various methods described above. Soft lithography especially has been used to pattern the surface of multilayers, and a variation on it, multilayer transfer printing, has been used to transfer patterned regions of entire multilayers. These and the other patterning methods for PEMs reported in the literature are generally limited to surface modification.

---

[1] Unpublished. ISCST shall not be responsible for statements or opinions contained in papers or printed in its publications.

Here we present the use of a modified type of micro-contact printing with hydrogel stamps, called reactive wet stamping (r-WETS) to pattern PEM films. With the r-WETS technique (developed by Grzybowski and coworkers) highly soaked hydrogels are used as stamps, and when placed in contact with the substrate the aqueous solution diffuses out of the stamp and into the substrate along the concentration gradient. This has been shown to be an effective way to deliver various aqueous solutions of salts, small molecules and acids or bases to be used to locally do chemistry or etch substrates such as glass with HF solutions. We have demonstrated that r-WETS can be an effective way to locally pattern PEMs in a number of ways. R-WETS can be used to deliver acidic or basic solutions can be used to create porosity in weak polyelectrolyte films such as poly(allylamine hydrochloride) (PAH)/poly(acrylic acid) (PAA) or linear poly(ethylene imine) (LPEI)/PAA, as well as to etch strong or weak PEM films using high ionic strength solutions. Local chemical reactions, such as the synthesis of metal nanoparticles, are also possible.

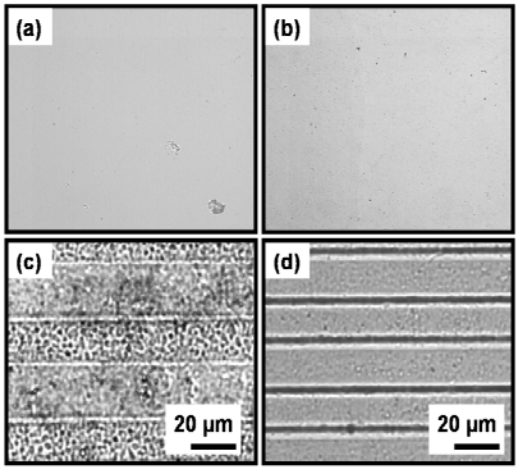

Figure 1. Optical Micrographs of a $(PAH/PAA)_{12}$ 8.5/3.5 film surface (a) as assembled, featureless PEM film (b) film after stamping with agarose line pattern soaked in neutral water, (c) $(PAH/PAA)_{12}$ 8.5/3.5 film after stamping with agarose line pattern soaked in pH 2.3 water, and (d) $(PAH/PAA)_{12}$ 8.5/3.5 film after stamping with line pattern soaked in 5M NaCl. Stamping PEM films with hydrogel stamps can etch the films as well as locally change film morphology.

As can be seen in Figure 1, the patterning achieved by r-WETS stamping of the PEM films can create features visible by optical microscopy. Figure 1 shows (a) a featureless, as assembled PAH/PAA multilayer, (b) a multilayer stamped with neutral water, (c) a PAH/PAA multilayer stamped with low pH water, and (d) a PAH/PAA multilayer stamped with high ionic strength solution. These images clearly demonstrate the creation of line patterns by r-WETS stamping, and specifically by the delivery of chemical reagents such as salt or acid, not merely by the application of pressure (fig 1(b)). In certain weak polyelectrolyte systems such as PAH/PAA, post-assembly exposure to low pH water will cause a porous morphology to emerge due to the change in protonation of charged groups and the breaking and reforming of ionic linkages within the PEM film. Although this transition from smooth film to porous has been previously reported, we are able to better observe it due to the slow rate of delivery of acid to the film. We are able to directly observe the onset of swelling in the PEMs, followed by what appears to be spinodal decomposition within the film, then the enlargement of pores, and finally collapse of the porous structure. With this process we are able to access a number of different pore morphologies with the same assembly and post-assembly conditions, but only varying stamping time. For example, application of a pH 2.3 soaked

hydrogel stamp for times less than 2 min results in patterned lines of smooth but swollen film, as can be seen in Figure 2. These raised, swollen features should be expected to have different mechanical properties, and also quite possibly different cell adhesion properties.

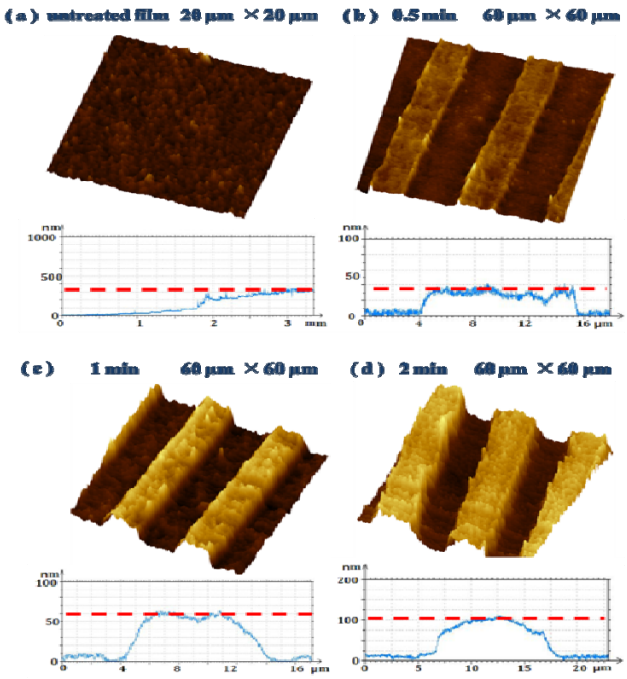

Figure 3. AFM images and profilometer scans (a) $(PAH/PAA)_{12}$ of unstamped LbL films (b) LbL films that had been stamped with agarose stamp for 30sec, (c) 1min, and (d) 2min

In addition to patterning physical properties we have also demonstrated the patterning of chemical properties. Changing the pH locally also changes the charge density, allowing for selective adhesion of charged small molecules such as fluorescein. Soaking the entire film in a metal salt such as silver nitrate and then using a stamp soaked in a reducing agent such as sodium borohydride allows for the local synthesis of metal nanoparticles within the film. Other reactions such as local crosslinking should be equally possible.

We demonstrate the use of r-WETS stamping for the patterning of polyelectrolyte multilayers. This technique has the ability to swell multilayers, etch them, and create localized chemical reactions in them. This method has not been previously used for the patterning of PEMS, and we believe that this method will present a powerful way to create previous unachievable architectures in these films.