Poly Acrylic Acid Patterning by Electron Beam Lithography

D. K. Brown
Institute for Electronics and Nanotechnology, Georgia Institute of Technology
Atlanta, GA
devin.brown@gatech.edu

Poly acrylic acid (PAA) is a polymer $(CH_2\text{-}CHCO_2H)_n$ and a derivative of acrylic acid that is a superabsorbent, being able to absorb and retain water, and swell many times beyond its original volume. This property classifies it into a group of polymers called hydrogels. Hydrogel volume is sensitive to environmental variables such as pH, temperature, ionic strength, analytes and biomarkers. Therefore, hydrogels are being investigated in emerging applications such as drug delivery, biosensors, tissue engineering, wound healing bandages, and more. The ability to lithographically pattern hydrogel materials to specific dimensions at the micro and nanoscale can be very useful in devices and sensors. Hydrogels based on poly(ethylene oxide) (PEO)[1], poly(vinyl methyl ether) (PVME)[2], and poly (N-isopropylacrylamide) (PIPAAm)[3] have been demonstrated to be sensitive to electron beam exposure, but there appears to be no work that has been published on the patterning of PAA hydrogel directly by electron beam lithography (EBL). In the development of nanoscale strain gauges, PAA was used as a sacrificial layer[4] and it was discovered at that time that PAA is sensitive to EBL. This work further investigates that discovery and presents the results of patterning PAA by EBL.

For process characterization, a 25% solution of 50,000 molecular weight PAA in water from Polysciences, Inc. was used. By further diluting with water, 12.5%, 8.3%, and 5.6% solutions were also prepared. These solutions were spincoated to achieve varying film thicknesses (Figure 1) onto Si substrates. Solutions below 25% required using an oxygen plasma beforehand to make the Si surface hydrophilic. A sample spin coated at 5000 RPM with 8.3% PAA solution, resulting in a 236 nm PAA film thickness, was exposed with 75 μm squares (Figure 2a) at varying doses at 1 nA and 100 kV using an Elionix ELS-G100 EBL system and then developed in water for 30 seconds. PAA exhibits negative tone behavior and has a base dose of ~75 $\mu C/cm^2$, overexposure beyond 100 $\mu C/cm^2$, and a relatively low contrast of 1.29 (Figure 2a,b). The thickness of the PAA at the base dose is 141 nm and is 95 nm thinner than the post-coat thickness. Varying line and dot array patterns were also exposed at 75 $\mu C/cm^2$ along with proximity effect correction (PEC) (Figure 3) resulting in minimum dimensions of 1.8 μm line widths and dot diameters both on 2.5 μm pitch with resolution limited by the low contrast. These results will be discussed in more detail along with other results. This work was partially supported by NSF Awards #1711259 and #1542174.

---

[1] P. Krsko, S. Sukhishvili, M. Mansfield, R. Clancy, M. Libera, Langmuir 2003, 19, 5618
[2] T. Schmidt, J.I. Monch, K.F. Arndt, Macromol. Mater. Eng. 2006, 291, 755–761
[3] V.R. Tirumala, R. Divan, L.E. Ocola, D.C. Mancini, J. Vac. Sci. Technol. B 23(6), 2005
[4] D. K. Brown, M. Kim, O. Brand, D. R. Myers, W. A. Lam, EIPBN, 2019, P1-25

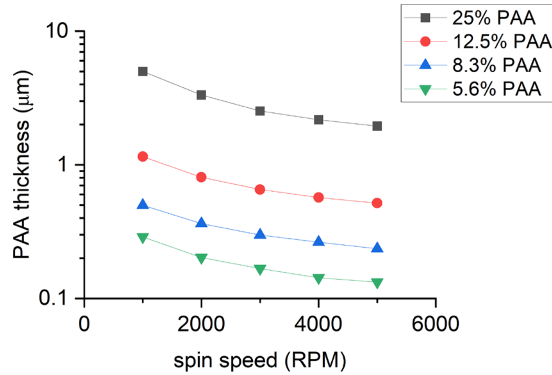

Figure 1: Log-linear plot of PAA film thickness versus spin speed for varying dilutions from 5.6% to 25% after 100 °C hot plate bake for 60 sec. Solutions below 25% require oxygen plasma pre-treated Si substrates.

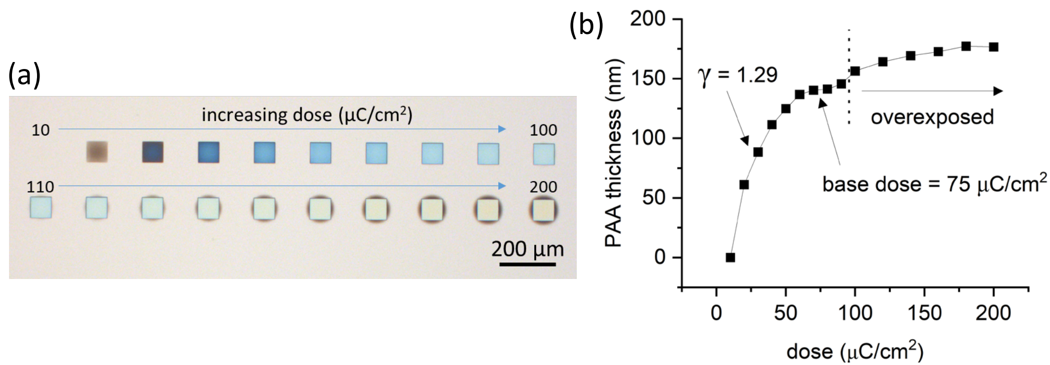

Figure 2: (a) Optical image of exposed 75 μm squares in 8.3% PAA spin coated at 5000 RPM (236 nm film thickness) on Si from 10 to 200 $\mu C/cm^2$ in steps of 10 $\mu C/cm^2$ after 30 sec H_2O develop, showing negative tone resist behavior. (b) Measured PAA film thickness of squares in (a) versus applied dose. Base dose is ~75 $\mu C/cm^2$ with PAA film thickness of 141 nm (95 nm less than original film thickness). Film thickness increases with dose, however, overexposure occurs beyond 100 $\mu C/cm^2$. The contrast, γ, is relatively low at 1.29.

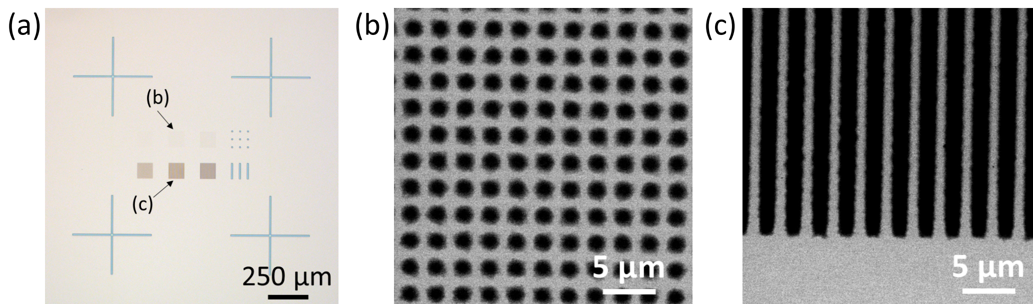

Figure 3: Pattern results of PAA by EBL at 75 $\mu C/cm^2$ plus PEC varying from 1.1 to 1.6X. (a) Optical image of four alignment marks surrounding four columns of dot arrays in top row and line arrays in bottom row. The smallest features to resolve are marked and shown in separate images to the right. (b) Electron micrograph image of array of 1.8 μm dot diameters (500 nm drawn) and 2.5 μm pitch. (c) Electron micrograph image of array of 1.8 μm lines (500 nm drawn) on 2.5 μm pitch. Bias of +1.3 μm from drawn to exposed caused by low contrast.