Bioinspired, Sequence-Defined Polymer Brushes as Patternable Surface Modification Monolayers for Semiconductor/Bio Interfaces

B. Yu, B. Chang, W. Loo, S. Dhuey, P. Ashby, M. Connolly, R. Zuckermann, R. Ruiz
Lawrence Berkeley National Laboratory, Berkeley, CA 94720
beihangyu@lbl.gov

P. O'Reilly
Molecular Vista, San Jose, CA 95119

K. Ryan, G. Tikhomirov
University of California, Berkeley, Berkeley, CA 94709

The ability to control and manipulate semiconductor/bio interfaces is key to enable biological nanofabrication pathways and new applications at the intersection of semiconductor technology and synthetic biology. Conventional surface functionalization strategies such as silane chemistries and self-assembled monolayers (SAMs) may offer only a limited level of customization for such interfaces, while polymer brushes offer a wider range of chemistries and maintain compatibility with lithographic techniques for engineering semiconductor/bio interfaces.

Here we developed a class of bioinspired, sequence-defined polymers–polypeptoids, as designer polymer brushes for surface modification of lithographic substrates. Polypeptoids with a hydroxyl group are designed and synthesized to enable efficient melt grafting onto silicon substrates, which form ~1 nm monolayers under lithographically relevant conditions. These polypeptoid brush monolayers are then patterned with electron-beam lithography to form well-defined surface patterns and are demonstrated to have maintained their chemical identity after the harsh conditions in the lithographic workflow. Chemical contrast patterns consisting of two polymer brushes (e.g., polypeptoid and poly(methyl methacrylate) brushes) are also generated using a similar workflow, with which we achieved selective adsorption of biomolecular building blocks such as DNA origami on the polypeptoid brush grafted regions. Furthermore, we demonstrate the adaptability of this platform for applications that involve semiconductor/bio interfaces by showing recent results on the tunable affinity to DNA origami of these polypeptoid brushes through monomer chemistry, as well as the capability to biotinylate these polypeptoid brushes. This surface modification strategy with bioinspired, sequence-defined polymer brushes allows monomer level control with a large parameter space of chemical functionality and monomer sequence, and therefore is a highly adaptable platform to precisely engineer semiconductor/bio interfaces.