Fabrication of Patterned Fluorinated and PEGylated Monolayer Surfaces for Fundamental Marine Fouling Studies

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Abstract:

Various designs for coatings that resist the attachment of marine organisms are based on the concept of “ambiguous” surfaces able to present both hydrophobic and hydrophilic functionalities as surface domains. Information is needed on the scale of the domains that the settling marine organisms are able to distinguish. To further this pursuit, silicon wafers were chemically modified to produce a pattern of squares containing alternating fluorinated and polyethylene glycol (PEG)ylated stripes of different widths on either a uniform fluorinated or PEGylated background. Each 1 cm × 1 cm square contained stripes with widths of 500, 200, 100, 50, 20, 5, or 2 µm as well as an unpatterned square with chemistry opposite that of the background. The integrity of the patterned monolayers was checked using protein adsorption and subsequent fluorescence microscopy and fundamental biofouling studies were carried out using the green alga Ulva.

Summary:

The fouling of ship hulls and other man-made marine structures is a significant problem that causes high operational and maintenance costs to industry [1]. Furthermore, these problems are being further exacerbated by the ever-rising cost of energy. In the closely related biomedical field, success in preventing fouling has been achieved using hydrophilic materials such as poly(ethylene glycol) (PEG) [2]. It is anticipated that PEG’s ability to resist nonspecific binding is through the formation of a hydration layer capable of hindering the nonspecific adsorption of proteins [3] and the adhesion of cells and microorganisms [4].

The green seaweed Ulva is a prominent fouling alga found throughout a wide range of marine environments. Distribution is chiefly through dispersion of microscopic zoospores, capable of settling on a solid surface [5]. Generally, a preference for Ulva to

Figure 1: Schematic diagram of the process used for creating alternating stripes of FOTS and PEG on silicon substrates using photolithography.

Figure 2. Diagram showing layout of chemically patterned Si wafer.
settle on hydrophobic versus hydrophilic surfaces has been established [6]. However, using this knowledge, fabrication of alternating PEGylated monolayers (PEG-SAM) and fluorinated monolayers on silicon presents an opportunity to probe the length scale at which the settling spores can discern the difference in hydrophobic and hydrophilic surface domains.

Alternating stripes of fluorooctyltrichlorosilane (FOTS) and PEG-SAM were produced on silicon substrates using photolithography. The overall process is depicted in Figure 1. Silicon wafers were first cleaned by immersion in piranha solution. Vapor deposition of FOTS was then performed using an applied microstructures vapor deposition system MVD-100 (1). The wafers were coated with Shipley S1818 positive-tone photoresist (2) and subsequently patterned using contact photolithography. (3). The patterns were developed using a Hemateach-Stega wafer processor (HMP900) (4), and subsequently subjected to oxygen plasma using a Harrick Plasma Cleaner (5). The patterns were then chemically backfilled using a PEG silane (6), and finally the photoresist was stripped (7) leaving the alternating patterns of PEG-SAM and FOTS.

Figure 2 demonstrates the layout of the eight patterned 1 cm² areas on the silicon wafer. 0 refers to a uniformly covered square of either PEG-SAM or FOTS opposite to the background. The number denotes square with stripes of FOTS and PEG-SAM of widths 2, 5, 20, 50, 100, 200 and 500 µm. The background is either pure PEG-SAM or pure FOTS.

The chemically patterned wafer surfaces were incubated with fluorescein-tagged BSA protein (BSA-FITC) in PBS buffer solution and then imaged using fluorescence microscopy. As depicted in Figure 3, protein adsorption was generally found to be significantly lower on the PEG-SAM regions of the patterns demonstrating the fidelity of the patterning process. Additional work found consistent behavior for settlement testing using Ulva zoospores above some threshold size (between 5 and 20 µm) at which the zoospores were no longer able to differentiate the surface domains [7]. Future work will be focused on exploring different shape features and also trying to further narrow down the domain size threshold at which the zoospores are no longer to differentiate the surface’s chemical properties. This includes, but is not limited to, checkerboard patterns as depicted in Figure 4.

References:

Figure 3, top: Fluorescence image from BSA-FITC adsorbed on the hydrophobic fluorinated region of a 2 µm patterned PEG-SAM square on a FOTS background.

Figure 4, bottom: Fluorescence image from BSA-FITC adsorbed on the hydrophobic fluorinated region of a 10 µm patterned PEG-SAM checkerboard on a FOTS background.