GRADIENT POLYMER BRUSHES
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Introduction
Substrates with gradient surface properties are interesting objects for investigation from both theoretical and practical points of view. The gradient surfaces have been successfully utilized in combinatorial methods of data collection in multiparameter space, substantially decreasing time and labor requirements. They have shown great advantages in the investigation of biological interactions along their length in one single experiment, allowing minimizing biological variations. The gradient surfaces also offer a plenty of opportunities to design responsive materials. On the other hand ultrathin end-grafted polymer layers are well known to affect dramatically the surface properties of substrates such as adhesion, lubrication, wettability, friction, and biocompatibility and, definitely, can be used to generate the gradient of properties on a substrate surface.

In the present work, we report the results of synthesis and characterization of gradient polymer brushes prepared from polymers covalently attached to the surface. The brushes were grafted to the surface through reactive poly(glycidyl methacrylate) (PGMA) layers.

Experimental
Highly polished single-crystal silicon wafers of {100} orientation (Semiconductor Processing Co) were used as a substrate. The wafers were first cleaned in an ultrasonic bath for 30 minutes, placed in a hot piranha solution (3:1 concentrated sulfuric acid/30% hydrogen peroxide) for one hour, and then rinsed several times with high purity water. Glycidylmethacrylate (Aldrich) was polymerized radically to give PGMA, $M_w=84,000$, $PDI=3.4$. Carboxy terminated polystyrene (PS) and poly-2-vinylpiridine (PVP) (Polymer Source Inc., Canada) were dip coated from methyl ethyl ketone solution. Wafers were annealed, with temperature gradient (160 – 200°C) created along the wafer. Unbound polymer was removed by multiple washing with hot toluene in Soxhlet extractor and rinsing in an ultrasonic bath. Ellipsometry was performed with a COMPEL automatic ellipsometer (InOm Tech, Inc.) and SENTACH Instruments GmbH scanning ellipsometer. Scanning Probe Microscopy (SPM) in tapping mode was performed on a Dimension 3100 (Digital Instruments, Inc.) microscope.

Results and discussion
PGMA anchoring layers prepared by dip coating were smooth and uniformly covered the surface. Scanning ellipsometry measurements showed uniformity of PGMA layer thickness on nanometric level (Figure 1). The thickness varied from 1.1 nm to ~1.6 nm on a sample area of 50 x 10 mm².

Wafers with PGMA thin layers were dip coated with carboxy terminated PS or PVP. Heating of the wafers from one side allowed creation of temperature gradient, which was translated into gradient in grafting density (Figure 2). Figures 3 and 4 show results of scanning ellipsometry measurements for grafted PS and PVP layers respectively. Measurements undoubtedly demonstrate formation of gradient polymer brush on the silicone wafer surface. PS layers thickness are varying from 1.5 nm to 8 nm on the distance of 20 mm. For PVP layers thickness changes from 6 nm to 10 nm on section with length of 30 mm.

Figure 1. PGMA thickness profile.

Figure 2. Preparation of gradient polymer brushes.
1 – Copper block preheated to the highest grafting temperature;
2 – Silicon wafer mounted by one end to the copper block;
3 – PGMA layer;
4 – Dip coated layer of carboxy terminated polymer.

Figure 3. PS gradient profile. X-axis length – 30 mm, Y-axis – 6 mm.

Figure 4. PS gradient profile. X-axis length – 30 mm, Y-axis – 6 mm.
Figure 5. SPM topography images of gradient polymer brushes. Vertical scale of all images – 30 nm. Image size – 1x1 μm.

PS and PVP gradient brushes attached at different grafting densities were studied by SPM operating in the tapping mode. Figure 5 presents topographical images of PS and PVP brushes. Uniform polymer layers were obtained at the edges of the gradient brush. On the areas corresponding to medium density of the grafting density, globular grafted structures were observed for both polymers. We connect such behavior with two competitive processes that occur simultaneously: i) grafting of the polymer molecules to the substrate; ii) dewetting of ungrafted polymer film. It is most likely, that at the cold end of the wafer, viscosity of the polymer is high, and the grafting occurs faster than dewetting. High rate of the grafting dominates over dewetting at the high temperature end. In the middle of the wafer two processes have approximately equal rate and dewetting occurs to a certain extent.

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