

# Surface Energy/Chemistry Gradients for Block Copolymer Thin Film Studies

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## INTRODUCTION

Self-assembling block copolymer materials provide an ideal route to engineering nanoscale features for emerging nanotechnologies. Applications such as nanotemplating,<sup>1-3</sup> filtration membranes,<sup>3-4</sup> organic photovoltaics,<sup>5</sup> and anti-reflection coatings<sup>4,6</sup> will require the use of block copolymers as thin films (~100 nm thickness), where self-assembly is highly influenced by surface energetics.<sup>1,7</sup> While over a decade of research has provided us with a general understanding of surface energy effects (e.g., on microstructure orientation), quickly and easily mapping the phase behavior of new materials for specific applications poses a challenge. Substrate surface energy/chemistry gradients provide us with a route to efficiently probe the effect of surface energy/chemistry on morphology. However, in order for this approach to be broadly applicable, the gradient fabrication method of choice needs to provide versatility in chemistry (i.e. functional groups), ease of implementation, and straightforward adaptability to new systems.

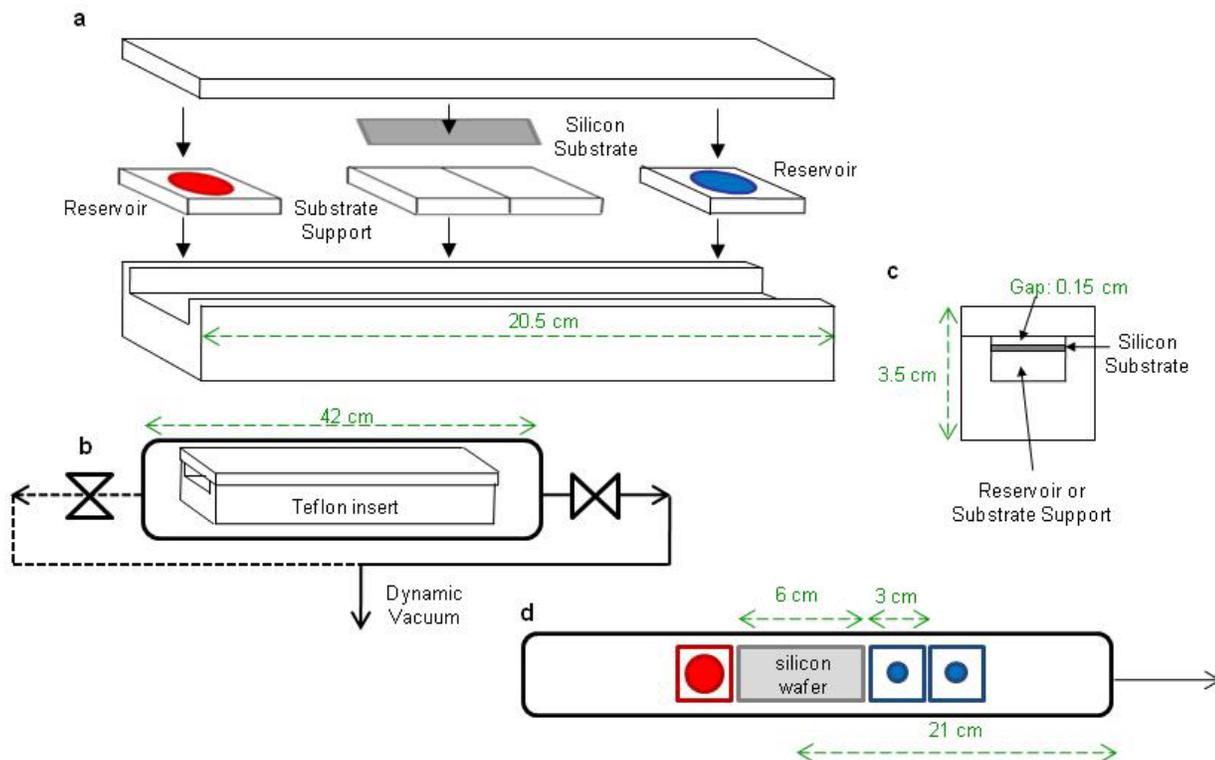
To meet this challenge, we have developed a single-step vapor deposition method for fabricating linear two-component gradients. In our method, functionalized monochlorosilanes are cross-deposited on to ultraviolet-ozone (UVO) cleaned silicon wafers under dynamic vacuum to generate a monolayer gradient. A custom-built Teflon

insert (Figure 1a-c) serves to confine the movement of the chlorosilane vapors to a small gap above the substrate surface, and the gradient profile can be tuned via the size and placement of the liquid chlorosilane reservoirs within the insert as well as vacuum directionality.<sup>8,9</sup> Chlorosilane functionalities are chosen based on the block copolymer of interest. Advantages of our method over others reported in the literature include: tunable, linear gradient profiles compared with steep sigmoidal profiles from traditional diffusion methods, simpler surface chemistry than polymer brush methods, and more versatility in surface chemistry (e.g. halogen, amine) than can be achieved with UVO methods.<sup>9,10</sup> In recently published work,<sup>9</sup> we used our gradient setup to generate a linear surface energy/chemistry gradient with functionalities suitable for a poly(styrene-*b*-methyl methacrylate) (PS-*b*-PMMA) block copolymer study, where one component is chemically similar to the PS block, and the other component is chemically similar to the PMMA block. We found the expected block copolymer phase behavior on our substrate surface energy/chemistry gradient, validating the utility of our gradient setup.

## EXPERIMENTAL

**General.** Certain commercial materials and equipment are identified in this paper in order to specify adequately the experimental procedure. In no case does such identification imply recommendation by the National Institute of Standards and Technology nor does it imply that the material or equipment identified is necessarily the best available for this purpose.

**Materials.** Benzyltrimethylchlorosilane (benzyl silane) and 3-methacryloxypropyltrimethylchlorosilane (methacryl silane) were used as received. Silicon wafers were rinsed with toluene, placed in a UVO cleaner for 1 h, and then rinsed again with toluene prior to use. Diiodomethane was used as received. Ethylene glycol was dried by vacuum distillation over sodium hydroxide and stored over molecular sieves in a desiccator under vacuum. PS-*b*-PMMA was obtained from Polymer Source, Inc. and had a molecular mass of  $M_n = 47,700$  g/mol and a PS volume fraction of  $f_{PS} = 0.77$  (calculated using homopolymer densities at 140 °C). The bulk morphology was hexagonally packed



**Figure 1.** Device schematic. (a) Reservoirs and substrate are loaded into the Teflon insert. (b) Insert is loaded into the deposition chamber. Deposition occurs under dynamic vacuum. Vacuum connections can be made on one or both sides of the chamber. (c) Gap between the substrate and the insert cover is small compared to the length of the insert. (d) Schematic representation of setup used to generate the gradient from benzyl silane and methacryl silane components. Adapted from ACS Nano.<sup>9</sup> [color online].

cylinders with a domain spacing of 24 nm.<sup>9</sup>

**Gradient Fabrication.** Linear gradients were fabricated using our device with one 1/2" (12.7 mm) diameter methacryl silane reservoir and two 1/4" (6.35 mm) diameter benzyl silane reservoirs, with the benzyl silane reservoirs located closest to the single vacuum outlet (Figure 1d).

**Contact Angle.** Water, diiodomethane, and ethylene glycol contact angles were measured using a First Ten Ångströms 125 contact angle measuring system with 2 µL drop size and the drop shape method for angle analysis. Surface energies were calculated using the Owens-Wendt method,<sup>11</sup> an extension of the Good-Girifalco geometric mean approximation,<sup>12</sup> which enabled calculation of the polar and dispersive surface energy components as well as the total surface energy.

**X-ray Photoelectron Spectroscopy (XPS).** XPS measurements were carried out at the National Institute of Standards and Technology on a Kratos AXIS Ultra DLD spectrometer at a vacuum of  $8 \times 10^{-9}$  Torr with a monochromatic Al source and a power of 140 W. A charge neutralizer was operated at a filament current of 1 A and a charge balance of 1.5 V to prevent sample charging.

**Block Copolymer Thin Film Preparation.** Uniform thickness block copolymer films were flow coated<sup>13</sup> on to the modified substrates from a 3 mass % solution of polymer in toluene. The films were  $\approx 70$  nm in thickness ( $2.9 \times L_0$ , where  $L_0$  is the bulk domain spacing), as determined by spectral reflectance using a Filmetrics F20 instrument. The films were dried by slowly increasing the temperature from room temperature to 80 °C and holding at 80 °C for 15 h prior to high temperature annealing at 170 °C for 24 h.

**Optical and Atomic Force Microscopy (AFM).** Optical microscopy images were collected on a microscope equipped with a CCD camera at 50x magnification. Tapping mode AFM images were collected on a Veeco Dimension 3100 atomic force microscope with a Nanoscope IV control unit.

## RESULTS AND DISCUSSION

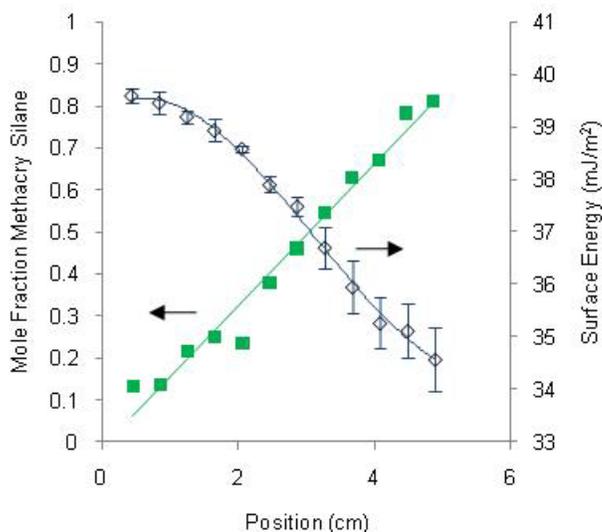
**Pure Component Monolayer Characterization.** The benzyl silane and methacryl silane monolayers were easily distinguished by their diiodomethane and ethylene glycol contact angles; therefore, these two probe fluids were selected for gradient characterization and surface energy calculations.<sup>9</sup> The pure component monolayers were further characterized by XPS and distinguished by their carbon 1s (C1s) spectra due to the carbon-oxygen binding in the methacryl silane. We fit the major components of these spectra to generate the overall envelope of each curve for subsequent gradient characterization.<sup>9</sup>

**Gradient Monolayer Characterization.** Using the vapor deposition method presented in this work, gradient monolayers were fabricated and tuned to achieve nearly linear surface energy and composition profiles across the substrate. Multiple points along the gradient were sampled for static contact angle (surface energy) and XPS (composition) characterization of the gradients (Figure 2).

Contact angle measurements indicated that the gradient spanned the length of the substrate (6 cm). Furthermore, from the benzyl silane end to the methacryl silane end, the diiodomethane contact angle increased nearly linearly and the surface energy decreased nearly linearly.<sup>9</sup>

The XPS C1s spectrum taken at each point along the gradient was fit as a linear combination of the two pure component spectra. From the relative contributions of each curve to the overall fit, we estimated the mole fraction of methacryl silane,  $x_m$ , at each point and found that the composition also changes linearly across the gradient.<sup>9</sup>

Both contact angle and XPS measurements confirmed that the gradient is primarily benzyl silane at one end (position  $\approx 0$  cm,  $x_m \approx 0$ ,  $\gamma_s \approx 40$  J/m<sup>2</sup>) and primarily methacryl silane at the other end (position  $\approx 6$  cm,  $x_m \approx 1$ ,  $\gamma_s \approx 34$  J/m<sup>2</sup>) with a linear profile in between.<sup>9</sup> Thus, the full range of surface energies/chemistries of interest were produced on a single substrate, yet the gradient was shallow enough that the surface energy/chemistry at any point was effectively uniform on the length scale of the block copolymer.

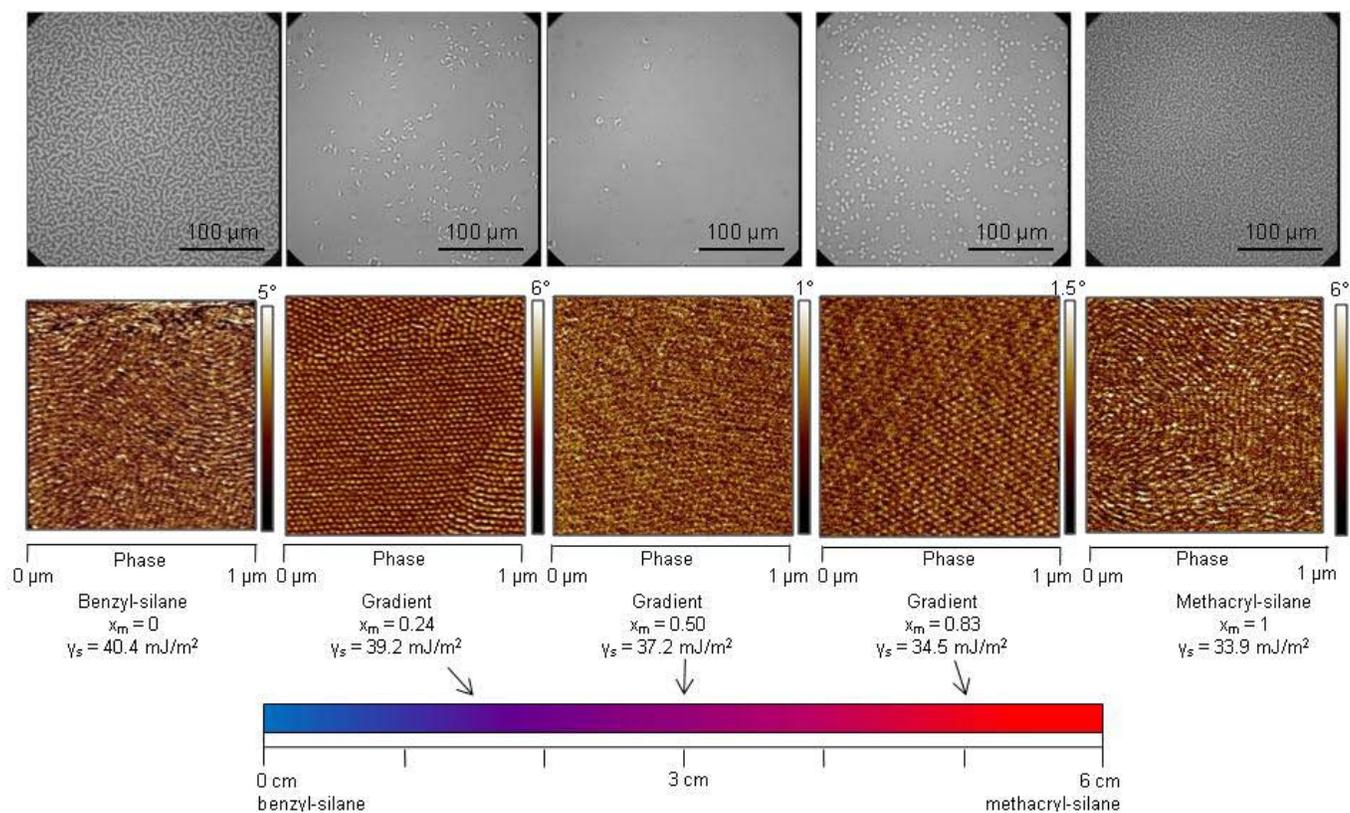


**Figure 2.** Composition (■), given by mole fraction of methacryl silane ( $x_m$ ), and surface energy (◇) characterization of the gradient. Error bars represent one standard deviation of the data from repeated measurements. Points without error bars represent a single data point. Adapted from ACS Nano.<sup>9</sup> [color online]

Also, because both the diiodomethane contact angle and the composition had linear profiles across the gradient surface, composition of a gradient point or mixed monolayer can be estimated from diiodomethane contact angle according to  $x_m = (\theta - \theta_b) / (\theta_m - \theta_b)$ , where  $x_m$  is the mole fraction of methacryl silane,  $\theta$  is the contact angle of a gradient point or a mixed monolayer, and  $\theta_m$  and  $\theta_b$  are the pure methacryl silane and benzyl silane monolayer contact angles, respectively.<sup>9</sup>

**Block Copolymer Thin Film Study.** Annealed PS-*b*-PMMA films demonstrated the expected phase behavior on the modified substrates (Figure 3). On the pure benzyl silane and pure methacryl silane monolayers, optical microscopy showed evidence of island/hole formation. AFM height images and sections (not shown) verified that the features observed optically were islands/holes. The corresponding parallel cylinder morphology was confirmed by AFM phase images.<sup>9</sup> The benzyl silane and methacryl silane surfaces are preferential for the PS block and the PMMA block, respectively, so parallel orientation of cylinders was expected.

Imaging at three points along the gradient sample showed that a wide range of monolayer compositions produced a relatively neutral substrate surface, leading to the formation of perpendicularly oriented structures. At a position 1.5 cm from the benzyl silane end of the gradient ( $x_m = 0.24$ ,  $\gamma_s = 39.2$  J/m<sup>2</sup>), the optical micrograph shows a few areas of island/hole formation, but is largely featureless. The microstructure orientation at this position was mostly perpendicular. At a position 3 cm from the benzyl silane end ( $x_m = 0.50$ ,  $\gamma_s = 37.2$  J/m<sup>2</sup>), the optical micrograph is essentially featureless and the microstructure is oriented perpendicular to the substrate surface. At a position 5 cm from the benzyl silane end of the gradient ( $x_m = 0.83$ ,  $\gamma_s = 34.5$  J/m<sup>2</sup>), we observe an increase in island/hole features in the optical micrograph as the surface becomes more preferential for the PMMA block. The microstructure orientation remains largely perpendicular, but regions that appear to be transitioning from perpendicular to parallel are present as well.<sup>9</sup>



**Figure 3.** Optical micrographs (top) and AFM phase images (bottom) of PS-*b*-PMMA thin films on pure component and gradient monolayer substrates. Adapted from ACS Nano.<sup>9</sup> [color online].

### CONCLUSIONS

We have developed a single-step vapor deposition method for generating two-component gradients with linear surface energy and composition profiles suitable for block copolymer thin film studies. In recently published work,<sup>9</sup> we used this method to generate a linear gradient consisting of benzyl and methacryl functionalities appropriate for examining the effect of substrate surface energy/chemistry on the self-assembly of PS-*b*-PMMA thin films. We identified the expected morphologies as a function of surface energy/chemistry in these films.

In preliminary work utilizing other chlorosilane functionalities, we have been able to fabricate gradients with a range of surface energies and chemistries (hydrocarbon, carbonyl, aromatic, fluorinated). The facile implementation and versatility in chemistry afforded by our method not only supports its utility for exploring block copolymer thin film self-assembly, but also gives it potential for application in studies of other surface phenomena, such as adhesion, wettability, and protein adsorption.

### ACKNOWLEDGEMENTS

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