

Combinatorial Mapping of Polymer Film Wettability On Gradient Energy Surfaces

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ABSTRACT

Combinatorial methods were used for studying dewetting of thin hydrophobic polystyrene (PS) and hydrophilic poly(*DL*-lactic acid) (PDLA) films on chemically modified gradient energy surfaces. Substrate libraries were prepared by immersing passivated Si (Si-H surface functionality) in Piranha solution (H₂SO₄/H₂O₂/H₂O) at a controlled rate, yielding a systematic variation of solvent contact angles across the surface. Additionally, chlorosilane-treated Si surfaces were exposed to UV radiation in a gradient fashion under ozone atmosphere such that a range from hydrophobic to hydrophilic conditions was obtained across the surface (≈ 3 cm). Solvent droplet contact angles of water and diiodo methane were used to quantify the spatial variation of surface energy along one axis across the surface. Libraries of thin films of PS or PDLA coatings on gradient energy surfaces orthogonal to gradients in film thickness were screened for dewetting behavior using automated optical microscopy. Contrasting trends in the wettability of PS and PDLA were visibly apparent as a function of surface energy of the substrate. The number density of polygons of the dewet PS films was found to obey a power law relationship with both film thickness and substrate surface hydrophilicity.

INTRODUCTION

Film stability and dewetting are important for applications in coatings ranging from photoresists, paints, adhesives, to lubricants, and biomaterials. Recently, much effort has been directed towards understanding the parameters that control the stability of thin polymeric films on solid substrates [1-6]. The parameters that influence film stability include substrate chemistry and roughness, time of equilibration, temperature of equilibration, polymer chemistry and molecular weight. Owing to the multivariable parameter space and the complexity of interactions between these variables, considerable theoretical and experimental effort has been directed towards understanding the physics of film stability on a substrate. Current experimental and theoretical literature of thin film stability on substrates only addresses chemically homogeneous Si or Silicon oxide substrates where the oxide film thickness is used to control the surface interaction [4, 7]. With the exception of recent theoretical work, the perturbing influence of surface energy gradients or quantification of the effect of surface energy on film stability has not been systematically studied [8].

We employ an approach to study the role of surface energy on film dewetting by etching silicon substrates with acid for different lengths of time. This approach provides a method to vary the strength of polar interaction on a single test substrate. However, the etching method may also induce roughness on silicon substrates that may also influence film stability. Alternatively, solvent deposition of the monochloro silane-coupling agent

followed by UV treatment under an ozone atmosphere may provide an approach for independently investigating the role of polar forces on polymer dewetting. It should be mentioned that this method eliminates complications from substrate roughness to overall film stability, as verified by Atomic Force Microscopy (AFM).

Combinatorial measurements provide an efficacious approach to study complex issues that involve multi-variables (i.e. surface energy, thickness, temperature) in a single experiment. The high-throughput nature of measurements on gradient energy substrates can be augmented by placing films with gradient in film properties orthogonal to the substrate gradient properties to obtain maps of the different substrate state and film property variables. Our study focuses on the combinatorial mapping of hydrophobic polystyrene (PS) film and hydrophilic poly d-lactic acid (PDLA) film on a chemical gradient energy surface obtained by either the etching technique or the chlorosilane/ UV ozonolysis combination method.

MATERIALS AND METHOD

The surface energy of Si was systematically varied by buffered oxide etching followed by an oxidizing “Piranha” ($\text{H}_2\text{SO}_4/\text{H}_2\text{O}_2/\text{H}_2\text{O}$) etch. In these studies, an “as received” silicon wafer (Polishing Corporation of America¹) was dipped in an aqueous HF/ NH_4F buffered oxide etch (J. T. Baker) for 3 min followed by 5 min in a volume fraction 40 % NH_4F aqueous solution (J. T. Baker) to produce a hydrophobic Si-H terminated substrate. The hydrophobically modified Si wafer was then gradually immersed into a Piranha solution (volume fractions of 30 % H_2SO_4 / 70 % H_2O_2) at controlled rates from 0.1 mm/s to 2 mm/s over a distance of 30 mm at 80 °C using a motion stage (CompuMotor). The substrate was then rapidly withdrawn from the solution, rinsed with deionized (DI) water, and blow dried with N_2 . This procedure creates a gradient in substrate exposure time to the Piranha solution to generate a gradient in the “degree of hydrophilicity”. Low molecular weight PS solutions were prepared (Goodyear, $M_w = 1900$, polydispersity = 1.19, glass transition temperature = (54 ± 1) °C with a standard uncertainty of 1 °C as determined by differential scanning calorimetry, where M_w is the mass average relative molecular mass) containing 2 % mass fraction PS in toluene. A fluid stripe of PS solution was spread over the gradient substrate under an angled knife-edge at constant acceleration to yield a thin film with a gradient in thickness orthogonal to the direction of the surface energy gradient. The film thickness was measured at different positions on the substrate with a UV-visible interferometer. The film thickness varied depending on the position of the substrate.

For creating a gradient energy surface with minimal roughness variation, precleaned silicon substrate was placed in chlorosilane solution for approximately 1 h, after which they were dried at 90 °C under vacuum for a minimum of 1 h. Chlorosilane - treated Si surfaces were exposed to a gradient in UV radiation under ozone atmosphere such that a range from hydrophobic to hydrophilic was obtained across the surface (length

¹ Certain commercial instruments and materials are identified in this paper to adequately describe the procedure. In no case does such identification imply recommendation or endorsement by the National Institute of Standards and Technology, nor does it imply that the instruments or materials are necessarily the best available for the purpose.

≈ 3 cm). Libraries of thin films of low molecular weight PDLA (Polymer Laboratories, $M_w = 10,000$, polydispersity = 1.19, glass transition temperature = $(54 \pm 1)^\circ\text{C}$) on gradient etched silicon substrates were prepared. A thermal gradient ranging nominally from 50°C to 100°C was applied orthogonal to surface energy gradient direction.

To estimate the surface energy of the substrate, spatially resolved static contact angles of water and diiodo methane were recorded using a Kruss goniometer. The polar component and the total surface free energy of substrate as a function of water contact angle were estimated using the geometric means approach of Owens and Wendt [9]. Libraries of thin films of PS or PDLA coatings on gradient energy surfaces were screened for dewetting behavior using automated optical microscopy.

RESULTS AND DISCUSSION

(A) Combinatorial Mapping of Dewet PS Film on Gradient Energy Surface

As-received silicon wafers are high-energy surfaces because they are usually covered with a thin layer (approximately 1 nm to 2 nm) of native SiO_x/SiOH . Passivating with an $\text{HF}/\text{NH}_4\text{F}$ solution replaces the oxide layer, with a “hydrophobic” Si-H surface. Figure 1 is a schematic representation of the chemical reactions that occur on a silicon wafer upon exposure to buffered solution and an oxidizing “Piranha” ($\text{H}_2\text{SO}_4/\text{H}_2\text{O}_2/\text{H}_2\text{O}$) etch solution. The reaction mechanism is comprehensively discussed in reference 10. The exposure of Si-H terminated wafer to Piranha solution results in the reoxidation of the Si substrate, the extent of which is dependent on exposure time to the Piranha solution. Gradual immersion of the passivated Si-H substrate into the piranha changes the exposure time of the substrate linearly across the surface. Figure 2 shows the water contact angle on the hydrophilicity gradient Si wafers as a function of position. Position $x = 0$ received the longest exposure to the Piranha solution. The water contact angle of the substrate, is sensitive to the composition of the Piranha solution and the immersion rate. Longer exposures of substrate to Piranha solution and higher concentrations of H_2SO_4 in the Piranha solutions led to lower water contact angles on the Si substrate, i.e., the substrate becomes more hydrophilic. Thus, substrate libraries with gradients in contact angle (θ) were thus prepared by immersing Si-H passivated Si in a Piranha solution ($\text{H}_2\text{SO}_4/\text{H}_2\text{O}_2/\text{H}_2\text{O}$) at a controlled rate.

Figure 3 presents optical microscopic images (cells) of the PS film on the gradient energy surface. The image represents selected regions of a combinatorial library in which film thickness and water contact angle of the substrate were systematically varied, while keeping the annealing temperature of the film constant. The water contact angle of the uncoated gradient energy surface varied from 40° to 60° (corresponding to surface energies of 45 mJ/m^2 to 35 mJ/m^2). The thickness of the polystyrene film was varied from 24 nm to 48 nm in the direction orthogonal to water contact angle.

Trends in the dewetted structure of PS as a function of film thickness (h) for constant water angle of substrate were compared to results reported in literature previously for non-combinatorial studies to validate the combinatorial method against conventional methodology. The results from conventional method were in qualitative agreement with the results obtained from combinatorial method. We performed a quantitative analysis of the dewetted structures by dividing the combinatorial library into

a virtual array of individual cells with various contact angles and thickness values. An automated batch program (NIH image) was used that allowed for the images to be thresholded and the calculation of the number of polygons, N_p , in the resulting voronoi pattern. Multiple regions of the sample were used for each measurement. The number density of polygons was found to obey a power law relationship, $N_p \sim h^{-4.3 \pm 0.2}$ at constant θ_{water} , in agreement with previous experimental results [1-3,12]. The -4 exponent suggests a possible capillary instability dewetting mechanism, as predicted by linearized capillary instability theory[11].

After validation of the high-throughput screening method by comparison to conventional studies of effect of thickness on dewetting, the study was extended to dewet structures on gradient energy surfaces. The number density of polygons of the dewet PS films was found to obey a power law relationship with substrate surface hydrophilicity at constant thickness (i.e. $N_p \sim \theta_{water}^{-3.6 \pm 0.1}$). The number density of polygons is larger for the more hydrophilic surfaces, with greater nucleation of dewetting sites suggesting unstable conditions for a PS film.

(B) Combinatorial Mapping of Dewet PDLA Film on Gradient Energy Surface

We extend the range of surface energy and decouple the effect of the polar component of surface energy on polymer dewetting by a gradient UV oxidation method. The change in polarity of the chlorosilane layer with UV radiation for different exposure times was measured by contact angles of multiple solvents on the chlorosilane layer. The polar and nonpolar or dispersion components of a substrate are calculated based on contact angle data and the polar and nonpolar components of surface tension for the two liquids. Surface tension values of 72.8 mJ/m² and 50.8 mJ/m² for water and methylene iodide, respectively, and the respective polar component values of 50.7 mJ/m² and 1.8 mJ/m² were used [12,13]. Longer exposures of substrate to UV radiation in ozone atmosphere led to higher surface energies. For example, the SAM layer oxidized for 5 min has greater surface energy than the unoxidized SAM layer and the 3 min oxidized SAM layer. The use of a fused silica optical density filter produces the same effect with regions with greater transmittance or dosage of incident UV being more hydrophilic. The optical density gradient of the filter thus produces a gradient in surface energy.

We prepared PLA film libraries in which temperature (T) and surface energy (γ) were varied systematically over the substrate in orthogonal directions. Figure 4 presents a composite set of images of the PDLA film on the gradient energy surface. The water contact angle of the uncoated gradient energy surface varied from 70⁰ to 40⁰ corresponding to respective surface energies from 30 mJ/m² to 50 mJ/m², while the endpoint temperature range used for this study ranged from 80 °C to 110 °C over 30 mm. This combinatorial map of the PDLA film was equilibrated for 6 h.

In conclusion, wettability gradients on Si substrates were used to map opposing trends in the stability of PS and PDLA films with surface energy. We validated the combinatorial method and found that the number of polygons of dewetted polymer was found to obey the relationship, $N_p \sim h^{-4.3 \pm 0.2}$ at constant θ_{water} which is in agreement with reported literature. A relationship between the water contact angle of the substrate and the number of polygons of dewetted polystyrene film at constant thickness (i.e. $N_p \sim \theta_{water}$

-3.6 ± 0.1) was established. PS dewets on the hydrophilic regions. PDLA films on gradient energy surfaces show contrasting behavior with the extent of dewetting increasing with increasing hydrophobicity (θ_{water}). Our results demonstrate that the late-stage dewet polymer pattern dimensions are sensitive to surface hydrophilicity, temperature, film thickness, and the relative polymer-substrate interfacial energy.

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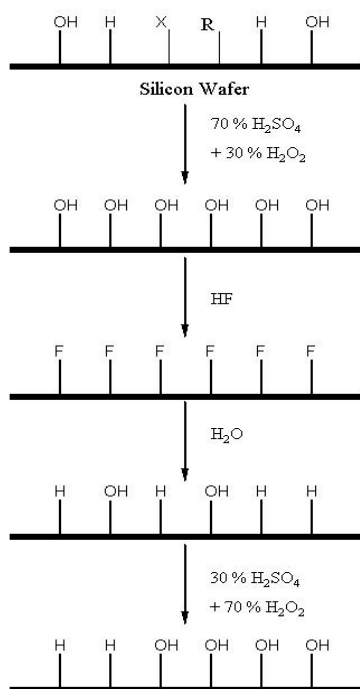


Figure 1. Schematic representation of reaction chemistry on Si wafer.

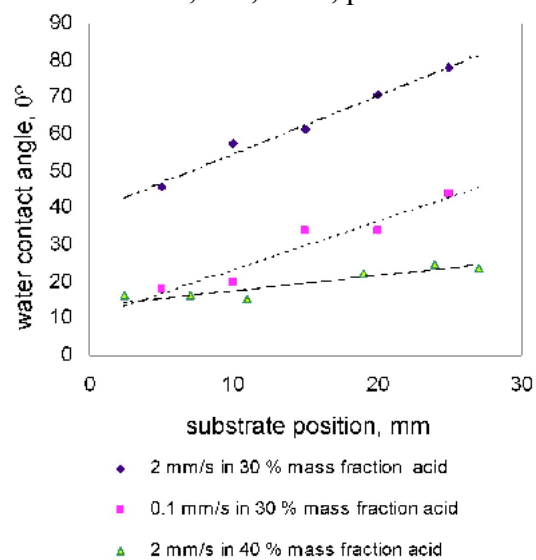


Figure 2. The water contact angle of passivated Si substrates as a function of position of substrate after exposure to Piranha solution. H_2SO_4 : H_2O withdrawal rate (◆) 30: 70 at 2 mm/s, (■) 30: 70 at 0.1 mm/s, and (▲) 40: 60 at 2 mm/s. Standard uncertainty is less than symbol size ($1\sigma \approx 1^\circ$). Straight lines are drawn to guide the eye.

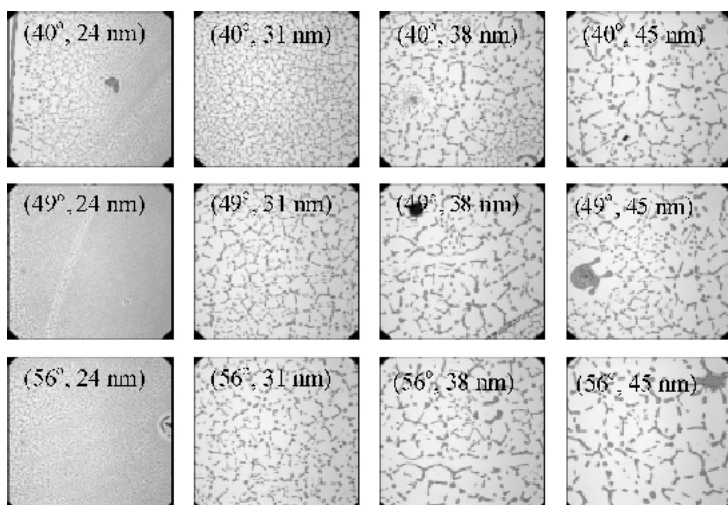


Figure 3. Composite of optical images of Si wafer for water contact angle/ thickness (θ , h) library of PS, $t = 2$ h, annealing temperature, $T = 100$ °C. ($760 \mu\text{m} \times 760 \mu\text{m}$)

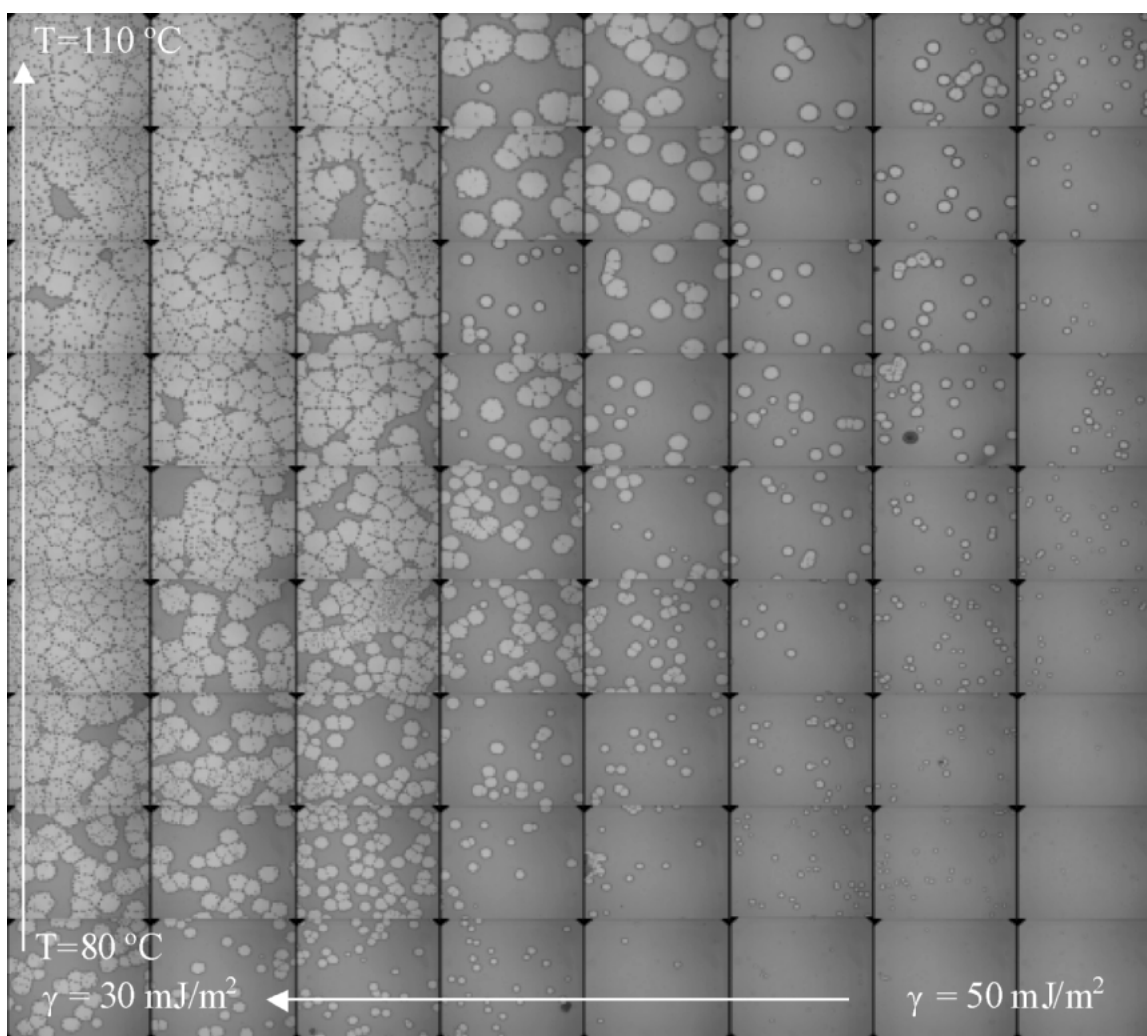


Figure 4. Combinatorial map of $\nabla\gamma$ vs. ∇T for dewetting of PDLA. $t = 6$ h, $h = 40$ nm. Montage of ($150 \mu\text{m} \times 150 \mu\text{m}$) optical images.