polymer

Combinatorial investigation of dewetting: polystyrene thin films on gradient hydrophilic surfaces

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Abstract

Film stability and dewetting is important to control for applications in coatings such as photoresists, paints, adhesives, lubricants, and biomaterials. We demonstrate the use of 2D combinatorial libraries to investigate thin film dewetting. Substrate libraries with gradients in contact angle (θ) were prepared by immersing Si–H passivated Si in a Piranha solution ($H_2SO_4/H_2O_2/H_2O$) at a controlled rate. Libraries of thin films of polystyrene on gradient etched silicon substrates containing orthogonal continuous variation of thickness were screened for dewetting behavior using automated optical microscopy. After comparing the high-throughput screening method to conventional studies of thickness effect on dewetting, a detailed morphological phase-map of the effects of contact angle on dewetting of polystyrene film was generated. Dewetting trends were visibly apparent. The number of polygons of dewetted polymer is sensitive to surface hydrophilicity as characterized by contact angle studies.
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1. Introduction

Thin polymer films find extensive technological applications in electronic, automotive, and biomedical coatings, as well as in packaging, adhesives, and paints. In most of these applications homogeneity, uniform thickness, and durability are essential. Thus questions concerning the stability of thin films on substrates is practically relevant. Current theoretical understanding of thin film stability on substrates is mostly limited to films on chemically homogeneous substrates and dewetting experiments on substrates considered to be chemically homogeneous often depart from theoretical predictions [1–4]. In this regard, ultrathin films may dewet by a process that resemble spinodal structures at early times [2,3]. While most experimental studies so far have dealt with thin liquid films on solid 'homogeneous' substrates, the more complex situation of a liquid dewetting from a chemically varying 'heterogeneous' substrate has received much less

attention [5]. The importance of chemical heterogeneity of the substrate is also manifested in the morphological templating of polymer blends on a chemically microprinted substrate [6]. The pattern-directed phase ordering results point to the importance of the chemical nature of the substrate and its interactions with components of the blend. These results point to the important role of localized heterogeneities such as particulates, the inhomogeneous oxide layer on silicon, and chemical contamination in determining film stability. While in many ways similar to surface heterogeneities, the perturbing influence of chemical gradients on film stability has not been visited, with the exception of a recent theoretical development [7]. As shown here, the task is complicated given the consideration of local heterogeneities within the gradient of the substrate and effects of film thickness on film stability. The breadth of parameter space and the complex interaction between these variables poses a challenge for investigation by conventional experimental techniques.

In this communication, we demonstrate the use of two-dimensional (2D) combinatorial libraries for studying the complex interaction of substrate chemistry and thickness on polystyrene film dewetting on Si substrate. Combinatorial methods, initially developed for pharmaceutical research,

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have received increasing attention for the synthesis, discovery, and characterization of novel catalytic, inorganic and organic materials [8–11]. These techniques provide a new paradigm for investigating complex phenomena involving multiple variables by executing many experiments in parallel. Four-basic steps are involved in the process: (i) experimental design, (ii) creation of sample 'libraries', (iii) high throughput screening, and (iv) data analysis or 'informatics'. In our case, informatics involves developing a 'phase-map' of dewetted microstructures as a function of both substrate chemistry (e.g. hydrophilicity) and film thickness.

2. Sample libraries

The experimental technique used to change the chemical nature of the solid Si surface, while keeping the surface relatively smooth, was buffered oxide etching followed by an oxidizing 'Piranha' ($H_2SO_4/H_2O_2/H_2O$) etch. In these studies, an 'as received' silicon wafer (Polishing Corporation of America[1]) 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 SiH terminated substrate. The hydrophobically modified Si wafer was immersed at controlled rates from 0.1 to 2 mm/s over a distance of 30 mm into a Piranha solution (30 vol% H_2SO_4/ 70 vol% H_2O_2) at 80 °C using a motion stage (Compu-Motor). The substrate was then rapidly withdrawn from the solution, rinsed with deionized (DI) water, and blown dry with N_2 gas. This procedure creates a gradient in substrate exposure time to the Piranha solution to generate a 'degree of hydrophilicity' gradient. The hydrophilicity of the gradient substrate was ascertained by measuring the contact angle of DI water using an automated contact angle apparatus (Kruss G2).

As-received silicon wafers are high-energy surfaces because they are usually covered with a thin layer (approximately 1–2 nm) of native $SiO_x/SiOH$ [12]. Passivating with an HF/NH_4F solution replaces the oxide layer, with a 'hydrophobic' Si–H surface. 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. Fig. 1 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 extent of surface oxidation, and hence the water contact angle of the substrate, is sensitive to the composition of the Piranha
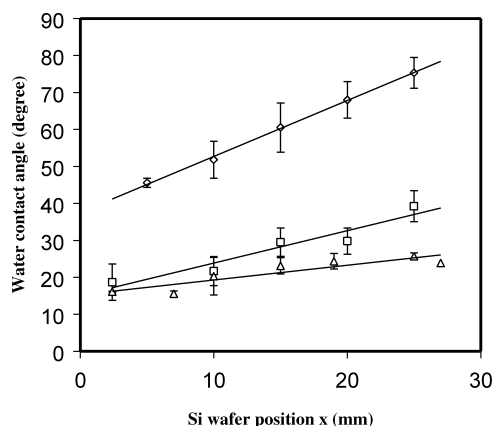
Fig. 1. The water contact angle of passivated Si substrates as a function of position of substrate after exposure to Piranha solution. H_2SO_4/H_2O_2 and withdrawal rate (◇) 30:70 at 2 mm/sec, (□) 30:70 at 0.1 mm/sec, (△) 40:60 at 2 mm/sec. The error bars represent 1σ.

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, e.g. the substrate becomes more hydrophilic. This is due to a higher conversion of Si/Si–H to $SiO_x/SiOH$, and growth of a thicker oxide layer for longer Piranha exposure times and higher H_2SO_4 concentrations.

3. High-throughput screening

Thickness gradients of polystyrene (PS) were prepared on the chemical gradient wafer with a velocity-gradient knife edge coating apparatus. Thin PS films were coated immediately after Piranha etching of substrate to minimize surface contamination and environmental moisture that could change the surface characteristics of the substrate. Low molecular weight PS solution (Goodyear, $M_w = 1900$, polydispersity = 1.19, glass transition temperature $= 54 \pm 1$ °C, where M_w is the mass average relative molecular mass) containing 2% by mass PS in toluene was prepared. A drop of the PS solution was spread over the substrate under an angled blade at constant acceleration to yield a thin film with a gradient in thickness orthogonal to the direction of the water contact angle gradient. The film thickness was measured at different positions on the substrate with a UV–visible interferometer employing a 0.5 nm light spot. The film thickness varied depending on the position of the substrate. Late stage dewetting was observed by annealing the sample at a constant temperature of 100 °C for 2 h, followed by collecting images with an automated reflection optical microscope.

4. Results

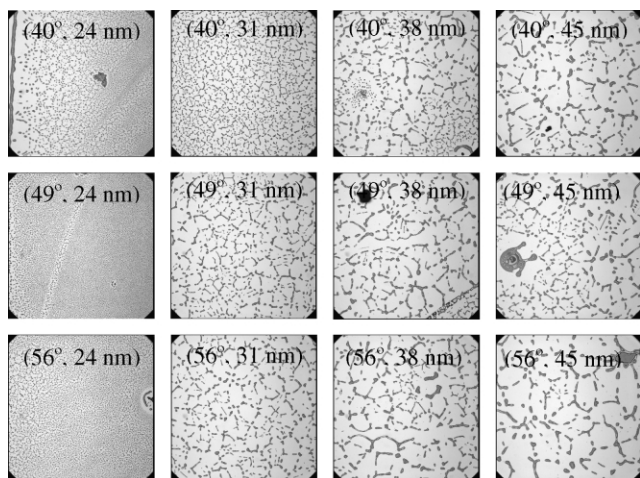Fig. 2 presents optical microscopic images ('cells') of the PS film at specified position on the gradient surface after

Fig. 2. Composite of optical images of Si wafer for water contact angle/thickness library of PS, $t = 2$ h, annealing temperature $= 100\,°C$. Image width is 0.76 mm.

annealing for 2 h. The picture represent selected regions of a combinatorial library in which film thickness and water contact angle of the Si substrate was systematically varied, while keeping the annealing temperature of the film constant. The water contact angle of the uncoated gradient surface varied from 40 to 60° and the thickness of the polystyrene film ranged from 24 to 48 nm in the direction orthogonal to water contact angle denoted, by the representation $[\theta\,(40, 60)°–h\,(24, 48)\text{nm}]$. It is important to note that the contact angle (θ_{water}) only varies by $\pm 1°$ within individual cells on the gradient library, because the cell dimensions are smaller than the water droplets used to measure water contact angle. Dewetting occurs by the growth of small circular holes that impinge to form small polygons within 2 h of annealing time. A predominant fraction of structures within any cell showed similar dewetted structural patterns (with the exception of few small patches on individual cells that have significantly different dewetted structural patterns dissimilar from the surroundings). We note that even within the similar regions, there are local variations (polydispersity) in dimensions of dewet patterns. We then treat the gradient library as a set of individual cells containing statistically significant data whose surface properties or potential are systematically different from the neighboring cell. Microscale wettability differences within a cell of the gradient library may cause a flow locally from the less wettable surface to a more wettable surface. However, in a previous study employing thickness-temperature library films [13] flow was not observed over macroscopic (mm) distances. However, microscale wettability heterogeneity can induce polydispersity in the final dewet structure by promoting heterogeneity in nucleation sites during hole formation [7]. These randomly distributed discontinuous polydisperse structures, which amount to a small fraction of the total surface, probably occur on the physical or chemical heterogeneities on the substrate surface that arise from non-uniform etching

during wafer preparation. The possibility of locally non-uniform etching rates of Piranha solution on the wafer surface may have contributed to these randomly distributed heterogeneous sites.

The results in Fig. 2 show distinctly varying dewet pattern dimensions at the inter-cellular level that are indicative of differences in film stability across the wafer. Trends in dewetted structure were compared to results reported in the 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. By using an automated batch program (NIH image), the images were thresholded and the number of polygons calculated. On average multiple regions of the sample were used for each measurement. The number of polygon for $[\theta\,(40, 60)°–h\,(24, 34)\text{nm}]$ was plotted as a function of film thickness at constant θ_{water} (Fig. 3a). As the film thickness increased, the number of polygons in the dewetted polymer film decreased. The literature suggests that when N_p varies as h^{-4}, capillary instability mechanism best describe film dewetting. While there is general agreement between our preliminary data and that of previously published results [1–4,13–15] with a capillary instability mechanism, we
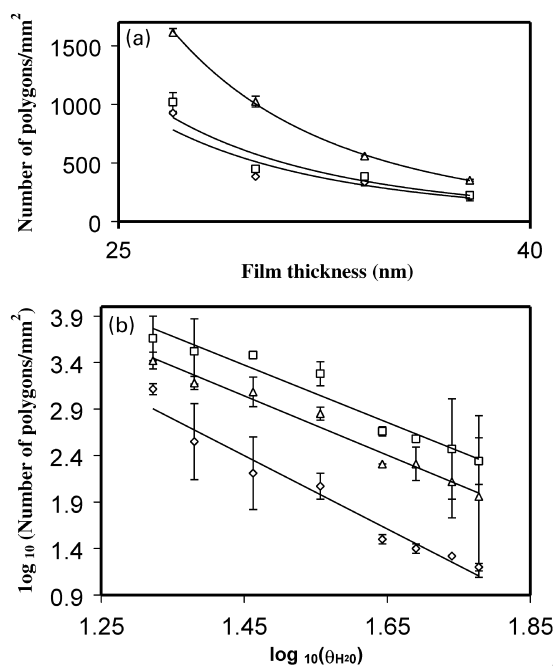

Fig. 3. Plot of (a) number of polygons versus thickness and ($\triangle$) 40°, ($\square$) 46°, ($\diamond$) 53°, contact angle of substrate. (b) $\log_{10}$ (number of polygons/mm^2) versus water contact angle of the Piranha treated passivated Si substrate. ($\triangle$) 34 nm, ($\square$) 43nm, ($\diamond$) 53 nm polymer film thickness. The error bars represent 1σ.

refrain from making a stronger point on this issue due to the limited h range and scatter in the data.

An important result of the present combinatorial study is the dependence of the number of polygons on the chemical nature of the substrate, as characterized by its hydrophilic character via water contact angle measurements. The number of polygons was found to be sensitive to the substrate surface hydrophilicity variation in addition to film thickness. Fig. 3b shows the areal number density of polygons (N_p) over the wide range of water contact angle at constant annealing temperature of 100 °C after 2 h. Double logarathimic plots fits to the data [$\theta\,(40, 60)° - h(24, 48)$nm] indicate that $N_p \sim \theta_{water}^{-3.6 \pm 0.1}$ for constant thickness strips. For the range of film thickness studied, the films are likely in the cross-over from capillary to heterogeneous nucleated regime [13]. The fact that the exponent is constant and not dependant on film thickness suggests that the chemical heterogeneity of the substrate affects film stability and dewetting independently of the film thickness effect in this cross-over thickness regime. The number density of polygons is larger for the more hydrophilic surfaces, suggesting a larger activation of nucleation sites under more unstable conditions. Despite the broad range of θ_{water} values considered (significantly more than that for typical hydrophilic surfaces (as in Fig. 3a)) dewetting occurs on these relatively lower energy surfaces. Recent publications indicate that chemical heterogeneities might destabilize films and produce unique morphological features [7]. In our case, the heterogeneity is assumed to arise due to a local change in the chemical nature and thickness of oxide layer, e.g. SiO_x and $Si(OH)_y$, on the silicon (high energy) wafer. At present, these film destabilization effects are not well understood, but it seems clear that a combination of equilibrium (i.e. polymer–surface interactions) and non-equilibrium (destabilizing heterogeneity on surface) conditions are involved.

Film stability studies have been commonly performed on substrates prepared to be chemically homogeneous. There have been few exceptions, where comparative study of polymer film dewetting on two or more discrete substrates with different surface energies have been performed [5,16]. At present, little is known about polymer film dewetting on chemically gradient surfaces. In this communication, we demonstrate a chemical etch method for creating a gradient energy surface on Si. The water contact angle (θ) of gradient surface ranged from 10 to 85° depending upon the exposure time of substrate to Piranha solution and the composition of Piranha solution. Our preliminary results suggest that the late-stage dewet polymer patterns (i.e. polygons) on chemically etched Si substrate are sensitive to surface hydrophilicity and film thickness. The novel but preliminary result of this communication is $N_p \sim \theta_{water}^{-3.6 \pm 0.1}$, where θ_{water} is the water contact angle of the substrate and N_p is the number of polygons of dewetted polystyrene film per unit area at constant film thickness.

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