GRADIENT MICROPATTERNS FOR SURFACE NANOMETROLOGY AND THIN FILM NANOMATERIALS DEVELOPMENT[‡]

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Introduction

Surface chemistry is an important parameter for next generation technologies, including nano-lithography masks, MEMS and NEMS, electronics packaging and photoresists.[1-3] In this work, we describe a simple technique, based on soft lithography,[4] chlorosilane vapor deposition, and graded UV-Ozone exposure to fabricate microscale chemical patterns that also exhibit a surface energy gradient. We are developing and using these specimens as a) reference substrates for nanometrology and b) as a platform for the high-throughput analysis of thin film behavior. In the first case, we demonstrate how gradient micropatterns can be used to calibrate image contrast and gauge probe quality in emerging Scanned Probe Microscopy (SPM) techniques such as Chemical Force Microscopy (CFM) and Atomic Force Acoustic Microscopy (AFAM). In addition, we demonstrate how graded pattern specimens can be used for the high-throughput analysis of surface-directed thin film dewetting. In particular, our graded specimens serve as model substrates to thoroughly and rapidly assess the effect of surface chemical heterogeneities (e.g. defects) on the dewetting behavior.

Experimental

We employed n-octyldimethylchlorosilane (ODS, Gelest, Inc[†]) to modify SiO_2 substrates.[5] A composite polydimethylsiloxane (PDMS, Sylgard 184) stamp, which is applied to a SiO_2-terminated Si substrate, and the stamp/substrate system is placed in a small vacuum desiccator along with a shallow boat containing ~0.5 ml of ODS. A low vacuum, applied to the desiccator, helps saturate the chamber with vapor. The chlorosilane vapor traverses the microchannels and reacts with areas of the substrate that are not physically masked by the stamp, thus forming a micropatterned Self Assembled Monolayer (SAM). After a vapor exposure of 1 h, the specimen is removed from the dessicator and the stamp is peeled away. Then the substrate is rinsed thoroughly with toluene and dried with nitrogen.

The chemical gradient is achieved via a graded UV-ozonolysis (UVO) of the SAM.[6] In the UVO method, the patterned surface is exposed to short-wavelength (184.9 nm and 253.7 nm) UV radiation through an aperture. Acceleration of the specimen beneath the aperture produces an exposure gradient, which gradually changes the chemical nature of the patterned SAM from hydrophobic (-CH3 terminated) to hydrophilic (-COOH terminated).

For the study of the effect of pattern contrast on polymer film wetting, a 35 nm polystylene (PS) film (Mw = 760 g/mol Cat No. 32782-4, Aldrich) was spin-coated from toluene onto a gradient micropattern library specimen and annealed in an oven at 60 °C for 24 h to accelerate dewetting.[7] Post-annealed film morphologies were measured by a custom-built automated optical microscopy (AOM) platform, and analyzed through automated image analysis.

Results and Discussion

Figure 1 illustrates the principles of our specimen design. The crux of the specimen is a "gradient micropattern" ($\nabla\mu p$): a series of micron-scale lines that continuously change in their chemical properties (*e.g.*, surface energy) compared to a constant matrix. Two "calibration fields" adjacent to the $\nabla\mu p$ directly reflect the chemistry of the lines and the matrix. Thus, traditional measurements (*e.g.*, contact angle) along the calibration fields gauge local chemical differences in the $\nabla\mu p$ and are used to "calibrate" domain contrast along the specimen.

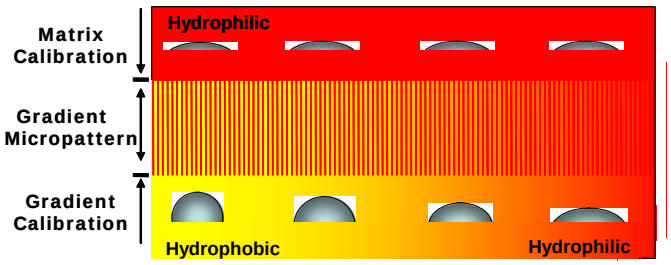

Figure 1. Schematic of gradient micropattern specimen, useful for SPM image contrast calibration and high-throughput analysis of thin film behavior. Chemical contrast along the gradient pattern (middle strip) is gauged via traditional measures along each calibration area (top and bottom strips).

Our $\nabla\mu p$ specimen is useful for quantifying image contrast in chemically sensitive SPM techniques such as friction-force SPM. In addition it can serve as a tool for gauging the quality and sensitivity of custom-funcionalized probes, such as those used in Chemical Force Microscopy. For example, Figure 2 demonstrates how our specimens can be used for calibrating friction force SPM image contrast. In this plot, the ordinate expresses the surface energy (γ) differences (between the graded lines and matrix) along the $\nabla\mu p$, derived from contact angle measurements collected along the calibration fields. The plot abscissa gives the friction force contrast between the lines and matrix for SPM images collected along the $\nabla\mu p$ area. Thus, from a single specimen we create a comprehensive calibration curve that relates SPM friction force to differences in surface energy. Moreover, the plot neatly illuminates the smallest γ-difference sensed by the probe, which is useful for gauging the quality of custom-made tips.[8]

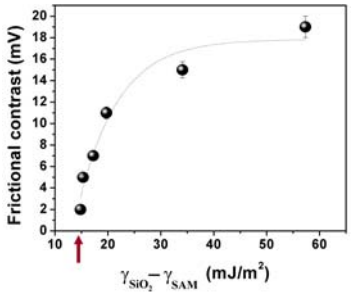

Figure 2. Calibration curve relating friction force SPM image contrast to surface energy (γ) differences between SiO_2 and UVO treated SAMs. This curve was derived from friction SPM images acquired along a gradient micropattern and contact angle measurements collected along the calibration strips. The red arrow shows the minimum γ-difference detectable by the SPM probe, i.e. its sensitivity. Error bars represent standard uncertainty. The dashed line is added to guide the eye.

The $\nabla\mu p$ specimens also hold great potential for the high-throughput analysis of thin film phenomena.[9] For example, we utilized the gradient micropattern substrate to investigate the influence of pattern size and surface energy contrast on the morphology of ultrathin dewetting PS films. In this way, the $\nabla\mu p$ acts as a model substrate for assessing the effect of surface chemical heterogeneities (such as defects) on the dewetting behavior. Our example specimen library encompasses a huge range of PS film dewetting behavior over the patterned area and flanking calibration fields. AOM analysis (1900 contiguous micrographs) and automated image analysis reveals several interesting trends. For example, as shown in Figure 3, strong chemical patterns (γ-difference about 15 mJ/mm^2) drive a surface heterogeneity-driven dewetting that results in well ordered arrays of PS microdroplets. In contrast, weaker chemical patterns (γ-difference about 5 mJ/mm^2) exhibit isotropic droplet polygons similar to those developed from random hole nucleation on homogeneous substrates. Because it expresses a comprehensive set of surface

[†] Certain commercial equipment and materials are identified in this document. Such identification does not imply recommendation or endorsement by the National Institute of Standards and Technology, nor does it imply that the products identified are necessarily the best available for the purpose.

energy differences, the gradient library enables precise determination of contrast regimes (e.g. for optimal droplet patterning) and critical contrast values, e.g., the weakest surface chemical heterogeneity needed to drive dewetting.

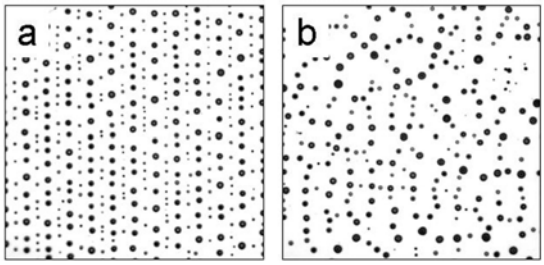

Figure 3. Optical micrographs of PS droplet morphology collected from two extremes of the ∇μp region of the film dewetting library. Micrographs are 0.5 mm wide. a) PS droplet patterning, which develops over regions with strong chemical contrast. b) Isotropic droplet polygons, which are exhibited over regions with weak chemical contrast.

Conclusions

We demonstrate the fabrication and use of a new type of substrate that combines micron-scale chemical patterning with a surface energy gradient. These gradient micropattern specimens are produced using a novel soft lithography technique followed by a graded UVO exposure that gradually modifies the chemistry of the patterned SAM along the specimen (from hydrophobic to hydrophilic). The utility of these specimens is demonstrated with respect to calibrating image contrast and gauging probe sensitivity in emerging SPM techniques such as CFM and AFM. In addition, ∇μp substrates hold potential for the high-throughput analysis of surface, interfacial and thin film behavior. We demonstrate this by using a ∇μp library to assess the effect of surface chemical heterogeneities on the dewetting behavior of PS thin films. Here, the gradient library illuminated trends, regimes and critical values useful to the engineering of thin film systems.

Acknowledgements

The authors thank the NIST MSEL Director's Reserve Program and the NIST Advanced Technology Program for Funding. Thanks also to Donna Hurley (Materials Reliability Division, NIST), Tinh Nguyen and Xiohong Gu (Materials And Construction Research Division, NIST) for providing feedback on our specimen designs, and to Jack Douglas (Polymers Division, NIST) for useful discussions.

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