

Mapping Wetting / Dewetting Transition Line In Ultrathin Polystyrene Films Combinatorially

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INTRODUCTION

Film stability of polymer coatings is important since "dewetting" exposes the underlying substrate and compromises the coating barrier properties. A number of recent studies have shown that the film stability and properties of bulk polymers can be vastly different from that of ultrathin films having a thickness h less than a thickness on the order of 100 nm to 200 nm (1-5). The changes in film properties (e.g., T_g and Debye-Waller factor) are natural since the film thickness h is becoming comparable to molecular dimensions and because the Van der Waals interactions with the substrate alters the chain conformations in the film relative to the bulk. The changes in film properties due to film thickness, along with substrate hydrophilicity / hydrophobicity, polymer relative molecular mass, and film preparation technique could significantly impact the film wetting characteristics; and we indeed find evidence suggesting that this is the case. Here, we present qualitative trends of a morphological "phase-map" for 30 nm PS film (for molecular masses ranging from 1,800 g/mol to 35,000 g/mol) equilibrated on substrates having orthogonal temperature and surface energy gradients.

EXPERIMENTAL

A self-assembled monolayer (SAM) was created by placing precleaned wafers in a solution with a mass fraction of 2.5 % of the octyltrichlorosilane (OTS; 97 % mass concentration) in toluene for 2.5 h. The monolayer was then rinsed with toluene and allowed to stabilize in a vacuum oven at 120 °C for at least 1 h. For creating a gradient energy surface, the SAM layer was exposed to a gradient in ultra-violet light ozone (UVO) atmosphere such that a range from hydrophilic to hydrophobic was obtained across the surface (≈ 3 cm). To estimate the surface free energy of the substrate, spatially resolved static contact angles of water and diiodomethane (99 % mass concentration, Aldrich Chemical Company) were obtained with the use of Kruss G2 / G40 contact angle goniometer.

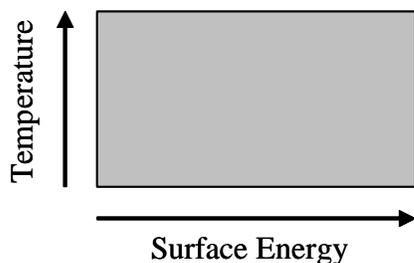


Figure 1. Schematic of combinatorial cross-gradients of surface energy and temperature. The surface energy gradient is created on the substrate surface while the temperature gradient is created by a stage, heated on one end and cooled on the other.

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A minimum of four measurements were then recorded for each liquid (at any spot) along different regions of the gradient energy substrate. The total surface free energy of substrate was estimated using the geometric means approach of Owens and Wendt (6).

Libraries of thin films of PS solution (Goodyear, $M_w = 9,000$ g/mol, where M_w is the average relative molecular mass) containing 2 % by mass PS in toluene was spun cast onto the gradient energy substrate. The film thickness was measured at different positions along the substrate with a UV/visible interferometer employing a 0.5 mm light spot and was found to be in the thicknesses range, $30 \text{ nm} < h < 40 \text{ nm}$. Similarly, PS films of molecular masses ($1,800 \text{ g/mol} < M_w < 35,000 \text{ g/mol}$) were cast on these substrates. Independently, the polymer samples were characterized for T_g by performing differential scanning calorimetry (DSC) measurements. Libraries of dewet PS film were prepared by applying a thermal gradient, ranging nominally from 85 °C to 150 °C, orthogonal to the surface energy gradient. Figure 1 shows the combinatorial cross-gradient exposure of the film to a linear temperature gradient and surface energy gradient.

At a predetermined time interval, the dewet polystyrene film was quenched to room temperature by removing the substrate from the hot stage and placing it on a copper block. The libraries were screened for dewetting behavior using a Nikon Optiphot-2 automated optical microscope and Tapping mode AFM.

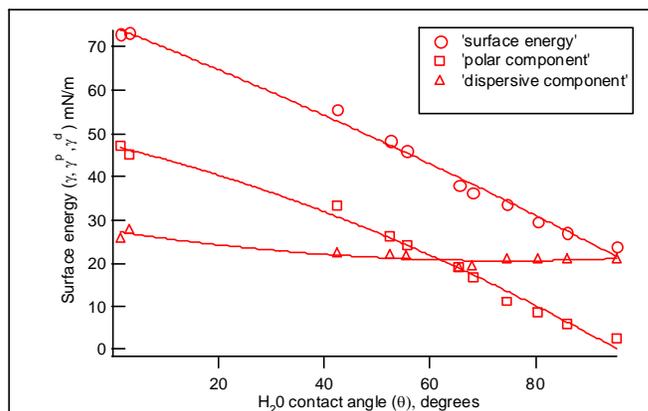


Figure 2. Measured surface energy gradients on a SAM substrate surface, treated with UVO with decreasing exposure time from left to right. The polar and dispersive values add up to the total surface free energy value. Standard uncertainty of the measurements is ± 5 %. Lines are drawn through the data to guide the readers eye.

RESULTS AND DISCUSSION

Substrate libraries with gradients in surface energy were obtained by the ozonolysis of a self-assembled monolayer by exposing the substrate to ultra-violet light for different lengths of time. A systematic decrease in the surface energy of the substrate was noticed, depending on UV exposure. The variation of the surface free energy of the sample mirrors the variation in polar component of the surface energy measurement, while the dispersion force component remains constant. Figure 2 shows the surface energy of the substrate on the gradient Si wafer as a function of water contact angle. It can be seen that the dispersion force component that relates to the van der Waals forces has remained nearly constant because the monolayer chains assembled are generally of equal length, while the polar component is varying with the extent of exposure of the substrate to ultra-violet ozone (UVO) treatment due to terminal group conversion (7). Figure 3 presents a collection of appended optical microscopic images of the PS film specimen taken at specified position to cover sub-regions (cells) on the gradient surface, after annealing the PS film for 50 min across 100 °C to 150 °C gradient. Although the combinatorial

map displayed in this figure was collected after 50 min annealing, similar dewetting trends were noticed even after about 500 min. We observe a reasonably well-defined wetting-dewetting transition line that separates regions of film stability from regions where the film dewets. The visual trend of a wetting - dewetting transition line observed for the PS relative molecular mass of 9,000 g/mol was similar to the trends observed for all other molecular masses (both above and below relative molecular mass 9,000 g/mol). Actually, the wetting- dewetting line is a narrow band of surface energies, and shown in Figure 3, the line is the median of this transition-region zone as a guide to the eye. Interestingly, the wetting-dewetting line is seen to curve in the morphological phase map over a wide lower T range, but ultimately plateaus at constant surface energy (SE) at high T.

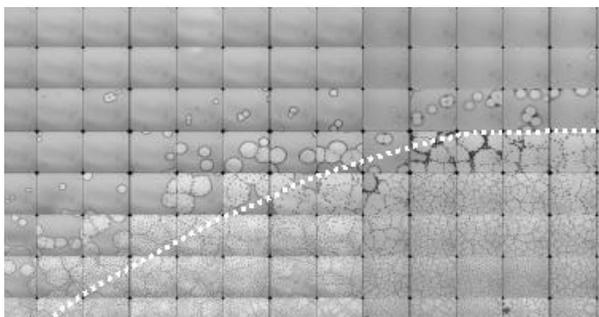


Figure 3. Wetting-dewetting transition line obtained by assembling a large number of images of a surface energy (SE) – temperature gradient (T) sample. The SE ranges from 25 mN/m to 50 mN/m from top to bottom of image, while T ranges from 100 °C to 150 °C from left to right end of image. PS had a relative molecular mass of 9,000 g/mol.

CONCLUSIONS

We have mapped a film stability line governing the transition between wetting and dewetting in ultrathin polymer films as a function of temperature and surface energy. The morphological phase map data suggests that film stability is sensitive to equilibration temperature, surface free energy of the substrate, and molecular mass of polystyrene. The wetting-dewetting transition line is non-linear with respect to annealing temperature.

DISCLAIMER

Certain commercial materials and equipment are identified in this article to adequately specify the experimental procedure. In no case does such identification imply the recommendation or endorsement by NIST, nor does it imply that these are necessarily the best available for the purpose.

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