Propagating waves of self-assembly in organosilane monolayers

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Circular waves of self-assembly

To demonstrate that the process of evaporating organosilane (OS) molecules from the diffusing source leads to centro-symmetric concentration profiles, we briefly consider generating circular waves of assembly by simply depositing a small drop (1 mm diameter) of the OS: paraffin oil mixture onto a wafer and letting the drop evaporate in the presence of air (Fig. 4). This has the effect of creating a high local concentration of OS on the wafer where the drop was deposited and this serves to initiate the wave of self-assembly from this surface inhomogeneity when the wafer is subsequently exposed to an OS source. The corresponding NEXAFS intensity maps of the OS (tF8H2 in this figure) concentration after 0.5 min and 1 min are depicted in Fig. 4a and 4b, respectively. As expected, the concentration of tF8H2 on the substrate is nearly symmetric about the position of the "nucleation site" and the qualitative nature of the wave propagation is similar to the numerical results for a circular FKE wave shown in Fig. 2c. The concentrations of the OS we report in the paper are normalized to a maximum concentration where the layer is fully formed and we refer to this dimensionless OS concentration as the surface fraction.

Growth of Self-Assembled Monolayers (SAM) in the absence of geometrical confinement

The SAM surface energy gradients described in the main body of the paper were all formed in a "confined geometry," corresponding to a small Petri dish (Fig. 5b). In addition, we have also prepared semifluorinated molecular gradients in an "unconfined geometry," where the source and wafer are enclosed in a relatively tall 2-liter beaker (Fig. 5a). As in the confined case, the "source" of OS was placed at the edge of the oxidized wafer substrate and the OS was mixed with paraffin oil (1:2 relative mass) to control the rate of evaporation (2). Exposing the substrate to the diffusing source for various times (ranging from 1 min to 20 min) produced OS concentration gradients on the exposed wafer. The resulting concentration profiles are show in Fig. 6. We then reduced the concentration profiles in the same manner as those shown in Fig. 3, i.e., the interface position $x$ on the substrate was rescaled as $(x-ct)/t^\beta$. Fig. 6b and 6d shows that best fits are obtained for $c = 0$ and $\beta = 0.50$ so that a constant velocity front does not arise. We suggest this apparent diffusive spreading of OS on the wafer represents a slower crossover from the short-time diffusive regime to the long-time constant velocity front propagation regime where the nonlinear terms in the reaction-diffusion equations predominate. At any rate, the unconfined system measurements provide valuable information about the diffusivities of the OS.
Fig. 4. Near-edge x-ray absorption fine structure partial electron yield (PEY) intensities collected from tF8H2 radial gradients prepared by placing a droplet of tF8H2 solution onto a flat silicon wafer: 0.5 min (a) and 1 min (b).
Fig. 5. Schematic illustration of the formation of self-assembled monolayer (SAM) surface energy gradients. Semifluorinated chlorosilane molecules are mixed with paraffin oil to control the rate of organosilane evaporation and this mixture is placed in a small container positioned at the edge of a silicon wafer subjected to a UV-ozone treatment. The evaporated chlorosilane molecules deposit on the wafer where the ordering process initiates from the edge of the wafer where the concentration is higher. The deposition is performed in two idealized geometries: (a) An "unconfined" geometry (placing a large beaker upside down over the organosilane source and wafer) or (b) A "confined" geometry (covering the OS source and wafer by a Petri dish). Elsewhere, we show that the average angular orientation of the molecules directly tracks the OS concentration. The normalized local concentration can thus be identified as an order parameter quantifying the extent of the SAM ordering.
Fig. 6. Time development of the frontal spreading of the fractional wafer coverage by mF8H2 and tF8H2 in an 'unconfined' geometry. The organosilane (OS) layers are formed as schematically indicated in Fig. 5a and fractional wafer coverage refers to the OS concentration relative to the fully ordered layer. (a and c) The local fractional wafer coverage of mF8H2 and tF8H2, respectively, as a function of the position $z$ on the substrate over a succession of times. (b and d) The same data as a and c, where the curves have been shifted in the $x$-coordinate to account for the constant velocity of the front movement, and where the width $w(t)$ of the front is divided by its time dependent width, $w(t) \sim t^{\beta}$, where $\beta = 0.5$. Lines represent the best fit to a tanh function (see main text), which can be derived as a leading perturbative solution to the FKE (1). This approximation is apparently robust.