

BEAMLINE
U7A

PUBLICATION

J.F. Douglas, K. Efimenko, D.A. Fischer, F.R. Phelan, and J. Genzer, "Propagating Waves of Self-Assembly in Organosilane Monolayers," *PNAS*, **104**, 10324-10329 (2007).

FUNDING

National Science Foundation

FOR MORE INFORMATION

Jack Douglas, Polymer Division
National Institute of Standards & Technology
jack.douglas@nist.gov

Jan Genzer, Department of Chemical & Biomolecular Engineering, North Carolina State University
jan_genzer@ncsu.edu

Progress in Self-Assembly: High Resolution NEXAFS Study of the Wave-like Growth of Self-Assembling SAM Layers on a Silicon Substrate

J. F. Douglas¹, K. Efimenko³, D.A. Fischer², F.R. Phelan¹, and J. Genzer³

¹Polymers and ²Ceramics Divisions, National Institute of Standards and Technology; and ³Department of Chemical and Biomolecular Engineering, North Carolina State University

Wavefronts associated with reaction-diffusion and self-assembly processes are ubiquitous in the natural world. Although it is often claimed that self-sustaining or autocatalytic front propagation is well described by mean-field "reaction-diffusion" or "phase field" ordering models, it has recently become appreciated from simulations and theoretical arguments that fluctuation effects in lower spatial dimensions can lead to appreciable deviations from the classical mean-field theory (MFT) of this type of front propagation. The present work explores these fluctuation effects in a real physical system. In particular, we consider a high-resolution near-edge x-ray absorption fine structure spectroscopy (NEXAFS) study of the spontaneous frontal self-assembly of organosilane (OS) molecules into self-assembled monolayer (SAM) surface-energy gradients on oxidized silicon wafers.

We examined the spontaneous self-assembly of organosilane molecules on an oxidized silicon surface. Upon exposure of the wafer to volatile source of the organosilane molecules placed to the side of the wafer in a closed container, a carpet-like layer spontaneously organizes from the edge of the wafer where the organosilane concentration is initially higher and this self-assembly process advances from the wafer edge at a constant velocity, ultimately covering the surface at long times (**Figure 1**).

By using high resolution X-ray synchrotron measurements in combination with simulation studies, we established that these wavefronts do not follow the constant width predicted by mean-field growth models

widely assumed to model such "self-propagating" or "autocatalytic" growth processes. Instead, the interface region separating the ordered and disordered regions became progressively rougher in time and this broadening was described

by a power-law growth predicted by previous simulation studies and theoretical arguments. The position of the wavefront is described by a relatively narrow interfacial region separating the ordered and disordered regions on the substrate that can be determined and tracked by NEXAFS measurements (**Figure 2**), which provide unique information about the density and ordering of the molecules on the surface. The novel aspect of this work is that the observations were being made for a real physical, rather than simulated, system.

Simple diffusion is not the process by which these SAM surface energy gradients fronts organize, as people had formally assumed. Unstable situations exist generically in the



Authors: (from left, top) Jack Douglas, (bottom) Frederick Phelan, (Group, from left) Jan Genzer, Kirill Efimenko, and Daniel Fischer

natural world and the emergence of new, more stable, patterns of behavior having a lower energy or competitive advantage is a rather universal 'evolutionary' process. By studying this type of process in detail through high resolution measurement, as exemplified by the NEXAFS study of growth of

SAM surface energy gradients, and by simulation studies, the group hopes to obtain insights into this fundamental growth phenomenon. This project offers the opportunity to compare the growth dynamics of the SAM layers with growth fronts found in numerous other (physical, biological and social dynamics)

contexts such as crystallization, the polymerization of actin and the frontal polymerization of synthetic polymers, the spread of diseases, tumor growth, wound healing, and the spread of languages, and agricultural practices.

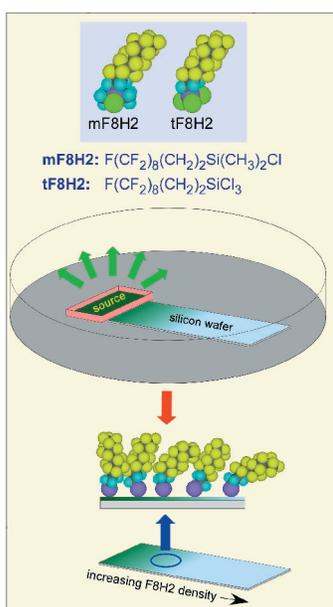


Figure 1. Schematic illustration of the formation of self-assembled monolayer (SAM) surface energy gradients. Semifluorinated chlorosilane molecules are mixed with paraffin oil to control the rate of organosilane evaporation and this mixture is placed in a small container positioned at the edge of a 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 a "confined" geometry (covering the OS source and wafer by a Petri dish).

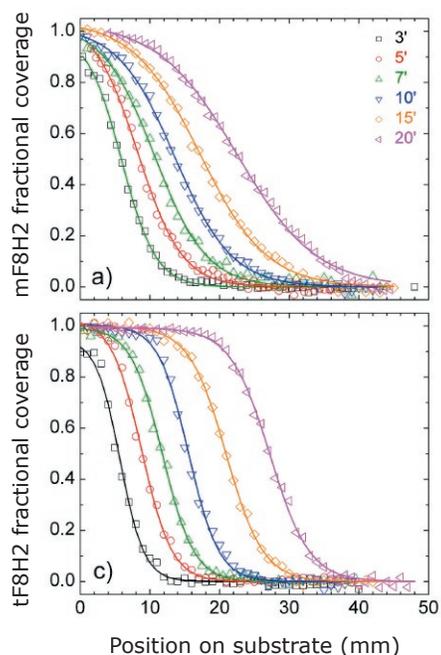


Figure 2. Time development of $mF8H2$ and $tF8H2$ surface energy gradients. The figures indicate $mF8H2$ and $tF8H2$ fractional coverage, respectively, as a function of substrate position for a succession of times. Fractional coverage refers to the OS concentration relative that for the fully ordered layer. Lines represent best fits to a hyperbolic tangent function as discussed in the original publication.