Self-assembly fronts in collision: impinging ordering organosilane layers†‡

Kirill Efimenko,a Ali E. Özçam,a Jan Genzer,*a Daniel A. Fischer,b Fredrick R. Phelan, Jr.c and Jack F. Douglas*c

Colliding autocatalytic wave-fronts of self-assembling organosilane (OS) layers are generated through the controlled positioning of sources of the volatile OS material at the edges of a silica wafer and through adjustment of the container dimensions in which the wafer sources are placed. The concentration profiles and molecular orientation of the OS colliding wave-fronts are assessed by means of combinatorial near-edge X-ray absorption fine structure (NEXAFS) spectroscopy. For systems involving self-assembly wave-fronts developing from the same OS precursor molecule, the shapes of interfacial region arising from front collision are centro-symmetrical and slowly ‘heal’ to form a uniform OS layer. In contrast, heterogeneous systems, involving OS molecules having different chemistries exhibit different rates of advance and highly non-symmetrical concentration profiles after front collision. We discuss the general nature of our OS colliding front data in terms of a mean field model of colliding reaction–diffusion fronts that generalizes a model introduced before for describing single OS front propagation.

Introduction

Reaction–diffusion (often termed “autocatalytic”) waves and the pattern formation associated with these waves represent ubiquitous phenomena in material science and biology. These autocatalytic waves exist in many diverse contexts, i.e., the introduction of foreign plant species into new environments,1 frontal polymerization,2 corrosion of metallic films,3 polymer dissolution,4 the growth of bacterial colonies,5,6 spreading of tumors,7 tumor growth,8 wound healing,9 frontal polymerization of actin10 and microtubules,11 wave-fronts of superconductivity,12 chemical reaction fronts,13 nerve propagation,14 flame propagation,15 virus proliferation in bacterial populations,16 polymer crystallization in confined spaces,17 and many others.18 In fact, many molecular processes can be described in terms of fundamental “entities” undergoing random local displacement events, which exhibit regular motion at large scales and associated pattern formation as the participating entities collectively move from some unstable state to a relatively stable state of greater energetic or competitive “advantage”. In material science as well as biology and social sciences, the key to successful application of these processes, leading to materials with desirable end properties and functions, is often associated with achieving a control of the growth process. This entails an understanding what factors control the rate of growth, the interaction between competitive growth fronts, interface evolution and responses of the fronts to changes in environment. Fluctuation effects tend to make these fronts increasingly incoherent (diffuse) in time,19 and thus are expected to greatly impact the interactions between frontal patterns under conditions where species (or different types of ordering) compete for supremacy.

In our previous work, we examined the spontaneous self-assembly of organosilane (OS) molecules on a flat oxidized silicon surface.19 Upon exposing the silicon wafer to a source of volatile OS molecules placed next to the side of the wafer in a closed shallow container (i.e., a Petri dish), a layer of self-assembled OS molecules organized spontaneously from the edge of the wafer where the OS concentration was initially higher and this self-organization process advanced from the wafer edge at a certain velocity, ultimately covering the surface at long times. By using high resolution X-ray synchrotron combinatorial near-edge X-ray absorption fine structure (combi-NEXAFS) spectroscopy, in conjunction with computer simulation studies, we established that these wave-fronts did 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 of the...
interface width ($w$) was described well by a power-law growth with critical exponents that matches those obtained by reaction–diffusion simulation studies and theoretical arguments based on field theory. The position of the wave-front was demarked by a relatively narrow interfacial region separating the ordered and disordered sections on the substrate that can be determined and tracked by combi-NEXAFS measurements, providing unique information about the density and molecular ordering in these monolayer materials.

The broadening of wave fronts implies that the way the fronts interact with one another and with boundaries (including obstructions in their placed in their path) will evolve in time. This is to say that the fronts ‘age’ inherently as they grow. In this paper, we study the collision between different types of OS fronts (e.g., different chemical species) to explore which type is thermodynamically “fittest” or “robust” (i.e., displaced the other and thus “survives”). The nature of the collision process is important to comprehend since the collision regions naturally give rise to whose properties that are related to device function and material stability. Specifically, we build upon our previous efforts and report on experiments involving wave-front formation in counter-propagating manner using two different classes of OS molecules, in which we systematically vary the OS chemical composition and the head-group chemistry that governs the attachment of the OS moiety to the substrate. The nature of the wave front interaction is discussed in terms of a general mean field framework for interacting reaction–diffusion fronts. We commence our experimental study of front collision by exploring the behavior in homogeneous systems, i.e., the same OS molecule but counter-propagating in direction. We then turn to heterogeneous set-ups involving the evolution of counter-propagating wave fronts made of OSs with different chemistries and head groups and address the roles of both the OS chemistry and the head group type in governing the formation of complex interaction between two interacting wave fronts.

**Experimental methods**

**Formation of gradients using OS front propagation**

We used four OSs comprising two different chemical compositions of the mesogen and two head-group chemistries. The OS molecules 1H1H2H,2H-perfluorodecyldimethylchlorosilane (mF8H2) and 1H1H2H,2H-perfluorodecyltrichlorosilane (tF8H2) were supplied by Alfa Aesar\(^{20}\) while phenethyl dimethylchlorosilane (mPES) and phenethyl trichlorosilane (tPES) were purchased from Sigma-Aldrich.\(^{20}\) All chemicals were used as received. Single-side polished, 300 µm thick silicon wafers with [100] orientation (Virginia Semiconductor, Inc.)\(^{20}\) were cut into (6 × 1) cm\(^2\) pieces and placed into an ultraviolet/ozone (UVO) cleaner (Jelight Company, Model 42),\(^{20}\) and exposed to the UVO treatment for 15 min in order to generate surface-bound –OH groups at the silica surfaces that served as attachment points for the OS molecules. The counter-propagating molecular gradients were formed by a variant of the method of Chaudhury and Whitesides.\(^{23}\) Equal amounts of respective OSs were mixed with mineral oil (ratio 1 : 1 or 1 : 5 by relative mass) and placed into Teflon containers separated by 6 cm and resting on the bottom of a Petri dish. The silicon wafer was placed between the two containers and the system was capped with the Petri dish lid. After a predetermined period of time the substrate was removed, washed copiously with ethanol in order to remove any physisorbed OS molecules and dried with ultra-high purity nitrogen.

**Formation of organosilane layer self-assembly waves**

Fig. 1 depicts the design leading to the formation of counter-propagating self-assembling waves and the chemical formulas of the OS molecules used in the experiments. Two OS sources are placed at the opposite edges of a 6 cm long silicon wafer. Because of high vapor pressure the OS molecules evaporate readily at ambient conditions forming a cloud of OS species in the vapor that traverses across the substrate and eventually gets deposited onto the substrate. Information about the competing nature of the fronts is obtained by carrying out the vapor depositions experiments for various deposition times.

The concentration and molecular orientation of OS molecules as a function of position on the substrate was assessed by means of near-edge X-ray absorption fine structure (NEXAFS).\(^{22}\) The NEXAFS experiments were carried out on the NIST/Dow Soft X-ray Materials Characterization Facility at the National Synchrotron Light Source at Brookhaven National Laboratory (NSLS BNL). NEXAFS spectroscopy involves the resonant soft X-ray excitation of a K or L shell electron to an unoccupied low-lying anti-bonding molecular orbital of σ symmetry, σ\(^*\), or π symmetry, π\(^*\).\(^{22}\) A measurement of the partial electron yield (PEY) intensity of NEXAFS spectral features allows for the identification of chemical bonds and determination of their relative population density within the sample. The OS molecules used in this work exhibit characteristic and distinct “chemical fingerprints” in their spectra: 1s → σ\(_{C–C}\) in PES (285 eV) and 1s → σ\(_{C–H}\) in F8H2 (292 eV). By collecting the PEY NEXAFS spectra at several sample orientations with respect to the incident X-ray beam, defined by the azimuthal angle $\theta$ between the sample normal and the polarization vector of the X-ray beam (20° ≤ $\theta$ ≤ 90°), the average surface molecular orientation of the OS self-assembled monolayer (SAM) molecules on the silicon oxide surfaces can be determined. In order to obtain information about the position-dependent concentration and molecular orientation of the OSs, we employed the “combi” NEXAFS set up,\(^{23}\) which is based on monitoring the PEY intensity while simultaneously rastering the sample across the X-ray beam (typical raster step was 0.5 mm). The PEY signal was collected at $\theta = 50°$, which is close to the “magic angle”,\(^{22}\) a geometry, in which the signal is independent of the molecular orientation. For selected specimens we also performed combi-NEXAFS experiments at $\theta = 20°$ and 90°. By combining the data collected at all three angles we could determine the average molecular orientation of the –(CF\(_2\))\(_n\)– mesogens on the surface.\(^{24-26}\) No attempts were made to measure molecular orientation in PES molecules because we know from our previous work that such systems exhibit only small degree of orientation.\(^{27}\) It is imperative to stress that the combi-NEXAFS set up minimizes any damages to the sample due to the X-ray and electron irradiation.\(^{28-30}\)
The PEY signals were collected for both carbon and fluorine K edges at the incident X-ray energies of 292 eV (carbon K edge) or 692 eV (fluorine K edge) for the 1s → σₓ-C–F signal and 285 eV (carbon K edge) for the 1s → σₓ-C–C signal. In addition, we collected signals at the carbon and fluorine K pre-edge (280 eV and 680 eV, respectively) and post-edge (320 and 720 eV, respectively). The PEY NEXAFS signals were normalized by employing the method of Outka and coworkers, 32 by subtracting the pre-edge signal from the 1s → σₓ-C–F or 1s → σₓ-C–C signals and scaled the post-edge to 1 for each spot on the specimen. The fractional coverage of OS molecules on the surfaces was calculated by normalizing the PEY NEXAFS intensities of the F8H2 and PES OSs in the gradient specimens relative to the PEY NEXAFS intensities collected from densely packed homogeneous self-assembled monolayers (SAMs) of tF8H2 and tPES. 27,34 The standard uncertainty of the NEXAFS molecular coverage and orientation is <5%.

Results and discussion

Self-assembly fronts from the same type of organosilanes

As a first step, we investigated the counter-propagation of OS fronts in homogeneous systems where wavefronts of OSs of the same kind were deposited from the opposite diffusing sources. In Fig. 2 we plot the fractional coverage of tF8H2 in tF8H2/tF8H2 system (left) and mF8H2 in mF8H2/mF8H2 set up. As expected, the profiles of each species are symmetrical in all specimens studied so far. A close inspection of the F8H2 concentration profiles reveals that at deposition times larger than 3 min the individual counter propagating profiles start to interact and overlap. A more descriptive picture of front interaction emerges when one plots the position of the diffuse front obtained by fitting the experimental profiles to tanh functions as a function of time. Fig. 3 depicts the fractional coverage of tPES in tPES/tPES system (left) and mPES in mPES/mPES arrangement. These results mimic those of the F8H2 species described earlier. In Fig. 4 we plot the positions of the wave-fronts for tF8H2, mF8H2, tPES, and mPES in their respective homogeneous counter-propagating fronts as a function of time. The data reveal that while tF8H2 fronts propagate relatively fast for the first ≈ 10 min of deposition, mF8H2 wave-fronts propagate at a slower pace. The latter behavior is also seen in homogeneous fronts involving ordering tPES and mPES OS molecules. What causes those differences in the wave-front propagation in homogeneous fronts? One possible explanation that can be put forward is the difference in the flux of the molecules that depends on the evaporation rate ultimately
depending on the vapor pressure (inversely proportional to the boiling point). Species with lower vapor pressure (i.e., higher boiling point) evaporate in smaller amounts and populate the SAMs on the substrate more slowly. One matter that complicates attributing this behavior solely to the flux of molecules in the vapor phase is the fact that OSs that possess tri-functional groups have a propensity to form larger complexes in the vapor phase (semi-fluorinated tri-functional species are particularly suited to form such well-stabilized complexes31) due to minute amounts of water vapor and also attach to the substrate more strongly because of their tendency to form intermolecular complexes at the substrate that are stabilized via inter-chain linkages connecting neighboring molecules.

More information about chain incorporation into the SAM wave-front can be obtained by monitoring the orientation of individual molecules using combi-NEXAFS. In Fig. 5, we plot the concentration (a) and molecular orientation (b) of F8H2 mesogen in tH8H2 homogeneous counter-propagating fronts. Note that in contrast to the experiments described previously, the concentration of the OS was reduced by diluting them with paraffin oil in the 1:5 ratio by relative mass. The data in Fig. 5 reveal, interestingly, that while the wave-fronts slow down considerably in developing due to interaction between molecules counter-propagating from two opposite directions, they are still mobile and as a result adjust their organization in the final assembly at a slower pace. The system is dynamic,

Fig. 2  (Left panel) Fractional coverage of tF8H2 in tF8H2/tF8H2 counter-propagating fronts as a function of the position on the substrate for various deposition times. (Right panel) Fractional coverage of mF8H2 in mF8H2/mF8H2 counter-propagating fronts as a function of the position on the substrate for various deposition times. In each plot, the light (grey) lines represent fits to the tanh function; the thick (blue) lines are the sums of the two counter-propagating tanh profiles. The fractional coverage is defined as the concentration of the given species relative to that of the respective organosilane in a dense homogeneous SAM layer.

Fig. 3  (Left panel) Fractional coverage of tPES in tPES/tPES counter-propagating fronts as a function of the position on the substrate for various deposition times. (Right panel) Fractional coverage of mPES in mPES/mPES counter-propagating fronts as a function of the position on the substrate for various deposition times. In each plot, the light (grey) lines represent fits to the tanh function; the thick (blue) lines are the sums of the two counter-propagating tanh profiles. The fractional coverage is defined as the concentration of the given species relative to that of the respective organosilane in a dense homogeneous SAM layer.
however, because of a non-zero molecular mobility (and presumably some surface diffusion) allowing virtually all molecules to reach their energetically preferred perpendicular orientation on the substrate as complete coverage occurs. For instance for the first 12 min of deposition the molecules tend to populate the middle part of the sample, but remain to be disorganized while the fronts collide. Only after the 15 min from the deposition time the molecules “find their space”, after reaching some critical concentration, that eventually leads to organized SAM. With increasing the deposition time the concentration of OSs in the colliding region increases, which results in better organization of the individual building blocks. The picture that emerges is that molecules arriving from opposite directions interact but are still far from reaching their equilibrium conformation. The rate at which the final molecular conformation is achieved is much longer than that it takes for the molecules to first come in contact. These observations give rise to a number of questions about what controls the

---

**Fig. 4** Positions of the wave-fronts in (a) tF8H2/tF8H2, (b) mF8H2/mF8H2, (c) tPES/tPES, and (d) mPES/mPES counter-propagating fronts as a function of deposition time. The dashed line depicts the position of the middle of the substrate. The values represent averages over 2–4 independent experiments, the error bars depict the standard deviation.

**Fig. 5** (a) Fractional coverage of tF8H2 and (b) average molecular orientation of the F8 mesogen, $\theta_{\text{F8}}$, in tF8H2/tF8H2 counter-propagating fronts as a function of the position on the substrate for various deposition times. The fractional coverage is defined as the concentration of the given species relative to that of tF8H2 in a dense homogeneous SAM layer. $\theta_{\text{F8}}$ depicts the average tilt angle from the surface normal.
dynamics of chain organization between the two diffusing fronts, whether it be the chemical nature of the molecules or the binding to the substrate. Clearly, more work needs to be done in order to clarify the observed behavior and we briefly consider a theoretical model of front interaction.

**Self-assembly fronts from different organosilane molecules**

In addition to the homogeneous front systems involving the same OS species, we briefly explore counter-propagation wavefronts where OS molecules of different chemistries and headgroups that are engineered to collide. In Fig. 6 we plot the concentrations of OS in heterogeneous systems involving families of two OS having the same chemistry but a different head-group (cf., Fig. 6 left panel) and different chemistry and the same head-group (cf., Fig. 6 right panel). These data suggest that after the collision (times >5 min) the frontal propagation slows down for both species. The profiles collected at longer times reveal that, in spite of a higher flux of the mF8H2 molecules given their lower boiling point and thus higher vapor pressure than tF8H2, the tF8H2 molecules penetrate the mF8H2 readily, thus pushing the mF8H2 front backwards, a behavior that is likely associated with molecular packing (which is better for tF8H2) and/or higher propensity of tF8H2 relative to mF8H2 to bind to the surface. This is clearly documented by the positions of the diffusing fronts plotted in Fig. 7a. Currently, we do not know which of these two effects is dominating. The chemistry and molecular density in the vapor phase may also influence the interaction between counter-propagating fronts. In the right panel in Fig. 6 we plot the fractional coverages of the two propagating tF8H2 and tPES wave fronts propagating in opposite directions during the collision phase of their interaction. Here the front penetration is seen at very short times, presumably because of higher flux of the tPES due to its higher vapor pressure (i.e., lower boiling point). With increasing time, the tF8H2 SAM seems to resist the penetration from tPES, but at long times the tPES front pushes the tF8H2 front slightly backwards, as shown by the positions of the wave-fronts plotted in Fig. 7b. The observed trends are not easy to interpret. It is

![Fig. 6](image1.png)  
**Fig. 6** (Left panel) Fractional coverage of tF8H2 (left ordinate) and mF8H2 (right ordinate) in tF8H2/mF8H2 counter-propagating fronts as a function of the position on the substrate for various deposition times. (Right panel) Fractional coverage of tF8H2 (left ordinate) and tPES (right ordinate) in tF8H2/tPES counter-propagating fronts as a function of the position on the substrate for various deposition times. In each plot, the light (grey) lines represent fits to the tanh function; the thick (blue) lines are the sums of the two counter-propagating tanh profiles. The fractional coverage is defined as the concentration of the given species relative to that of the respective organosilane in a dense homogeneous SAM layer.

![Fig. 7](image2.png)  
**Fig. 7** Positions of the wave-fronts in (a) tF8H2/mF8H2, and (b) tF8H2/tPES counter-propagating fronts as a function of deposition time. The dashed line depicts the position of the middle of the substrate. The values represent averages over 2–4 independent experiments, the error bars depict the standard deviation.
likely that the front tendency to "push" their counter-propagating neighbors stems from complex interplay between the molecular flux, tendency to form stable clusters in the vapor phase and propensity to bind to the surface. In the next section, we perform model calculations of front collisions to gain some insight into our novel OS front collision observations.

General model of colliding autocatalytic fronts

We develop a general framework for describing the collision of our fronts based on generalization of a model used before successfully for individual OS fronts. To establish the model, we first consider a pair of planar reaction–diffusion equations as in our measurements and with various idealized assumed interactions between the resulting simulated fronts.

First, we consider the reference equations describing the extent of local ordering \( \Phi \) for the two species A and B and we denote these 'order parameters' as \( \Phi_A(x) \) and \( \Phi_B(x) \) to establish our notation. Taking these fronts to initiate from the left and right edges of our rectangular wafer, our governing reaction–diffusion mean field equations for \( \Phi_A(x) \) and \( \Phi_B(x) \) in the absence of interaction are then,

\[
\frac{\partial \Phi_A(x)}{\partial t} = D_A \nabla^2 \Phi_A(x) + k_{1A} \Phi_A(x) - k_{2A} \Phi_A^2(x),
\]

(1)

\[
\frac{\partial \Phi_B(x)}{\partial t} = D_B \nabla^2 \Phi_B(x) + k_{1B} \Phi_B(x) - k_{2B} \Phi_B^2(x),
\]

(2)

where \( D_a \) denotes the species order parameter diffusivity in the context of OS layer ordering. The rate constant \( k_{1a} \) describes the rate at which the i species is generated (ordering occurs) and \( k_{2a} \) is a second order reaction parameter describing self-interaction of the A and B species. The ratio of the rates \( k_{1A} / k_{2A} \) governs the ultimate level of growth of order \( \Phi_A(x) \), or the amount of chemical species generated through this reaction process, and we have chosen our normalization of parameters to correspond to \( \Phi_A(x) \) taking a value of 1 for a fully saturated reaction. This is an obvious choice when \( \Phi_A(x) \) is interpreted as an order parameter. \( \Phi_A(x) \) and \( \Phi_B(x) \) are also taken to equal 1 to the left and right of the rectangular plate edges and both of these order parameters are initially 0 (no OS ordered layer initially exists) within the plate domain, the boundary condition for the front propagation. In the absence of spatial heterogeneity, where the \( \nabla^2 \Phi_A(x) \) terms vanish, this is just the classical 'logistic equation' of population growth, a reasonable model for population growth in the US and many other contexts. Other models of reaction models involving higher order reactions or even polynomials in \( \Phi_i(x) \) can be considered, but such changes do not alter essential aspects of the front propagation, at least within mean field theory.

Fig. 8a illustrates the propagation of a single wavefront \( \Phi_A(x) \) from the left to right corresponding to eqn (1) with \( D_A = 0.01 \) and \( k_{1A} = k_{2A} = 1 \). Each front can be well described (after a short transient during which the front builds up) by the simple propagating kink solution, \( \Phi_A(x) = (1/2) [1 - \tanh(x - ct)/w] \), where \( c \) is the front velocity and \( w \) is the front width.

Fig. 8b we shift the numerical solutions from Fig. 8a by transforming the \( x \) axis in this figure to a coordinate system moving with the front interface position (inflection point of curves in Fig. 8a) with a velocity \( c, x \to x - ct \). The curves superimpose very well, apart from a short time transient. Despite the simplicity of the reaction–diffusion model, it provides a reasonable description of our propagating OS data for individual fronts. In Fig. 8c, we show some illustrative data for fractional coverage of tF8H2 (i.e., tF8H2 concentration relative that for the fully ordered tF8H2 layer) for various front propagation times. The data is obtained by the same combinatorial near-edge X-ray absorption fine structure (NEXAFS) spectroscopy methods as in the present paper. The tF8H2 2 front in position in this figure has been shifted in time to account for the constant velocity of the front movement, as in simulation studies shown in Fig. 8b. The solid line indicates the tanh function \( \Phi_A(x) \) indicated above, but there is an important difference from the simulated front propagation, the front width \( w \) broadens in time as power law, \( w \sim t^{0.28} \). (This interfacial broadening exponent is consistent with theoretical estimates from field theoretical arguments and this phenomenon is discussed at length in ref. 19.) Apart from the front broadening phenomenon, the mean field reaction–diffusion model clearly captures the essential nature of the front propagation and the reduced variable description of the front evolution is very well fit by the reaction–diffusion model.

While the simple Fisher–Kolmogorov equation [eqn (1) for an individual front] serves as a useful framework for modeling of front propagation under remarkably general circumstances, it does not allow a description of front interaction and the front aging (interfacial broadening) phenomena relevant to our measurements. Some simple physical observation motivate the introduction of a similarly generic model of mutual front interaction, but we leave the matter of modeling the frontal broadening to a future occasion since our first goal is understand qualitative aspects of front collision and interaction. As a first step in this direction, we show two idealized planar fronts \( \Phi_A(x) \) in Fig. 8d of the same species A that propagate and collide where there is no mutual interaction [reaction terms are the same as in the single front (Fig. 8a) even as the fronts collide] between the fronts arising from the interaction between distinct chemical species. In our measurements, we can achieve this situation by simply considering two fronts involving the same OS molecules though the positioning of the OS sources at opposite sides of the silicon wafer. Fig. 8 shows the dynamics of this ideal type symmetric collision process. The impinging A fronts \( \Phi_A(x) \) first propagate as if the other did not exist, they then stop propagating upon collision and the interfacial region gradually 'heals' until the ordering is uniform at long times, there being no trace of the propagating fronts at earlier times. This simple case captures some qualitative aspects of the measurements described above (Fig. 6), but this simple non-interacting model does not capture the interfacial asymmetry that we observe in the collision between two fronts populated by distinct OS molecules. We next introduce a generalized coupled reaction–diffusion model to describe front interaction underlying this observed asymmetry in the interfacial region of the colliding fronts of distinct species.

We take the general form of the reaction–diffusion equations describing the interacting fronts to be the same as eqn (1).
and (2), but the reaction terms of species A in eqn (1) can be expected to be renormalized by the presence of interacting B species. The primary effect of this mean field interaction should be to alter the generative rate parameter $k_{1A}$ (the rate of OS ordering in the present context) and we can reasonably expand the effective $k_{1A}(T)$ of the interacting fronts in a Taylor expansion in both $\Phi_A(x)$ and $\Phi_B(x)$. In the spirit of Landau theory of phase transitions, where similar free energy expansions are formally invoked, we keep the leading constant term (the non-interacting reference system), a leading term linear in $\Phi_A(x)$ that quantifies the decreased rate of species A self-generation due to the presence of B and a cross-term $\Phi_A(x)\Phi_B(x)$ describing an interaction between A and B species localized to a region where the distinct front types overlap:

$$k_{1A} = k_{1A,\text{bare}}[1 - \delta_{1A}\Phi_B(x) - \delta_{2B}\Phi_A(x)\Phi_B(x)],$$

(3)

$$k_{1B} = k_{1B,\text{bare}}[1 - \delta_{1B}\Phi_A(x) - \delta_{2A}\Phi_A(x)\Phi_B(x)],$$

(4)

where $\delta_{1A}$, $\delta_{1B}$ and $\delta_{2A}$, $\delta_{2B}$ are dimensionless coupling parameters describing the strength of these self and mutual interaction frontal interactions where $k_{1A,\text{bare}}$ and $k_{1B,\text{bare}}$ are the ‘bare’ self-generation rates of A and B, respectively, in the absence of any front interaction. The mutual interaction term $\delta_{2A}$ can also be thought of in terms of how the self-competitive interaction rate parameter $k_{2A}$ is altered by the presence of B so that are accounting to the leading order species B perturbations that alter $k_{1A}$ and $k_{2A}$. To have the general equations of motion for our fronts to be invariant to species, we simply permute A and B to obtain our definition $k_{1B}$. Of course, the coupling parameters describing the front interaction $\delta_{1A}$, $\delta_{2A}$, $\delta_{1B}$ and $\delta_{2B}$ are now variable and this gives the fronts their specific ‘identity’. We next illustrate some idealized limiting situations that lead to classification scheme for ‘canonical’ types of front collisions.

First, we illustrate this frontal interaction in the case where the interaction only involves the leading term ($\delta_{1A} = \delta_{1B}$) associated with the basic generative rate. For simplicity, Fig. 9 shows fronts of two species (A and B) that propagate from the right and left, respectively, in a profile representation to aid in the visualization where we take $\delta_{1A} = \delta_{1B} = 1$ and $\delta_{2A} = \delta_{2B} = 0$. These fronts show only a weak interaction until they impinge,

![Image](image_url)
whereupon the fronts cease their advance, as in the non-interacting front in Fig. 8d. The arrested interface develops a progressively sharp profile for both A and B, but this interface never heals at longer times; each front simply refuses to budge after initial colliding and coming to a steady position with respect to each other. We call this a *symmetric front collision* since neither front can gain advantage over the other and the fronts remained locked in position in perpetuity.

Another extreme situation corresponds to a case where the species B strongly inhibits the generation of A, while at the same time, the species A has a much more limited effect on the generation of species B so that that B is the ‘fitter’ species. We may then expect the B species to eventually displace A and the frontal wave collision must then evolve rather differently than in the *symmetric front collision*. To illustrate this presumably common situation (it is a way of evolution in nature for one species to ultimately displace another), we take, $\delta_{1A} = 1$, $\delta_{1B} = 0$; $\delta_{2B} = 0$, $\delta_{2B} = 0$ and Fig. 10 confirms the displacive nature of these B fronts. At early times, before front collision, there is little interaction between the fronts, but upon colliding, the B front simply annihilates the A species. We term this an *annihilating front collision*.

Finally, we consider the case where the generative capacity of the A species occurs through an interference term that is linear in both $\Phi_A(x)$ and $\Phi_B(x)$ so that the B species dominates the A population, reducing its productive through *mutual interference* rather than directly annihilating A. In this case, we may expect the A and B species to come to some mutual accommodation in their populations. To illustrate this situation we take, $\delta_{1A} = 0$, $\delta_{1B} = 0$; $\delta_{2A} = 1.5$, $\delta_{2B} = 0$ and show the result of two colliding fronts having the parameter values indicated in Fig. 11. In this case, the B fronts runs over the A front after collision, but in this case the A and B populations come to equilibrium values determined through their mutual interactions associated with their mutual coexistence. We term these *coexisting front collisions* where one of the populations is subsidiary to other species of reasonably similar type. Notably, the A species still manages to persist after the invasion. In this way, waves and waves of populations can pile upon each other, leading to diversity in the resulting coexisting populations. Human population genetics and other biosystems almost certainly reflect processes of this kind.

We see from above that the interaction between the fronts can lead to quite different situations where the fronts collide

---

**Fig. 9** 'Symmetric Front Collision'. A and B reaction fronts collide where they symmetrically affect each other's generative rate resulting in front pinning after collision. For simplicity, we take $D_A = D_B = 0.01$ in eqn (1) and (2) and the front interaction parameter values, take $\delta_{1A} = \delta_{1B} = 1$, $\delta_{2A} = \delta_{2B} = 0$ defined by eqn (3). The boundary conditions at the onset of front development are the equivalent of those in Fig. 5a. (a) Wavefront approach; (b) initial collision; (c) post collision relaxation to equilibrium; and (d) equilibrium collision profile. Note that the interface does not heal at long times as in the non-interacting collision series shown in Fig. 8b.
and become stationary, collide where one front annihilates the other and where one front simply adsorbs the other. Although the cases just illustrated are extreme situations of interacting fronts, the frontal interacting types illustrate some distinct patterns of behavior to be expected in our measurements of colliding OS fronts. We next discuss our results within this general theoretical framework.

**Comparison between experiment and modeling**

We use the general systems identified in the modeling section to compare to our experiment. While the parameters used to model the colliding fronts are only phenomenological, some general conclusions between the experimentally observed and modeled fronts can still be made. First, the colliding fronts featuring the same organosilane species (cf., Fig. 2–4) depict the characteristics of the symmetric front situation. That is, upon collapsing the front position remains constant and the fronts only broaden and eventually collapse given enough time. More interesting situations occur when either the head-group or the mesogen structure in the counter-propagating organosilane species are varied. Let us consider the former situation. tF8H2 and mF8H2 counter-propagating fronts reveal a clear shift in the front position that moves from the center towards the mF8H2 species. Considering that the flux of mF8H2 is likely slightly higher than that of tF8H2 (the normal boiling points of mF8h2 and tF8H2 are 198 and 224 °C, respectively), and that the mesogen structure in both species is identical, one can attribute this behavior to the effect of the head-group in the organosilanes. The tF8H2 molecule possesses 3 potential attachment points relative to only 1 present in mF8H2. Moreover, the tF8H2 molecules can form a stable SAM that is stabilized by the formation of in-plane linkages among neighboring tF8H2 molecules. In contrast, mF8H2 only attaches to the surface by a single bond and is significantly tilted due to the present of two bulky methyl groups. It thus appears that the differences in the head-group structure of the two organosilanes are responsible for the behavior that resembles closely that of the annihilating front collision. One may speculate that the behavior is due to the fact that F8H2 is three-times more likely to bond to the surface relative to mF8H2. Moreover, the closer molecular packing and in-plane linkage stabilization in tF8H2 contributes to the higher stability of the SAM relative to mF8H2. Finally, we consider the case of the tF8H2 and tPES counter-propagating fronts. Here,
the head groups are identical in both molecules. From the experimental data, it appears that the tPES front outperforms the tF8H2 front, but the F8H2 molecules persist and are not displaced altogether. This situation would correspond to the coexisting front collision situation depicted in the computer simulations; both fronts propagate while one of them takes over without completely displacing the other. From a molecular-level perspective, one can argue that given the same structure of the head group, the observed behavior can be attributed to the larger flux of the tPES molecules relative to that of tF8H2 (the normal boiling points of tF8H2 and tPES are 224 and 95 °C).

While these observations are preliminary, they reveal that the wave-fronts in homogeneous systems are symmetrical while those in heterogeneous systems originating from different species are no longer symmetrical, in qualitative accord with the model simulations. In order to explore these systems more systematically, one would need to vary systematically the flux of the diffusing molecules in the vapor phase using the aforementioned dilution methods. We now see that we should probably initiate the fronts at greater initial distances apart so that the fronts fully develop before colliding. Computer simulations using the model described earlier provide important molecular details of the processes involved in wave-front propagation and interaction. By judiciously choosing the combination of the diffusivities and the equilibrium rate constants for the autocatalytic reaction for each front, “invasion waves” can be generated, which either annihilates or displaces to some degree the other front. It would be interesting to generate such interacting fronts to provide molecular-level understanding for such behavior, which also has clear implications to studying the evolution and competition of biological species (e.g. biofilm growth, competition between healthy and cancerous tissues, growth of engineered tissues in a matrix of healthy tissues, etc.).

Conclusions

We studied the interaction between two colliding autocatalytic wave-fronts. These wave fronts are formed by letting organosilane (OS) precursors evaporate and travel in vapor phase in counter-propagating directions. Upon landing on a flat...
silica-based surface the organosilane get immobilized and their concentration profiles and molecular orientations are assessed by combinatorial near-edge X-ray absorption fine structure (NEXAFS) spectroscopy. Two types of profiles are studied that include homogeneous systems (counter-propagating waves are made of the same OS molecule) and heterogeneous systems (counter-propagating waves are composed of OSs with different chemistries and head-groups). While in the ‘homogeneous species’, where each OS molecule is the same, the concentration profiles of both waves are centro-symmetrical, the spreading fronts of heterogeneous systems composed of competing ‘species’ have a different character, the wave-fronts sometimes lead to symmetric and other times asymmetric profile fronts in regions where the fronts are colliding and thus strongly interacting. Ongoing work aims at providing molecular details of the observed behavior by means of a computer simulation model that includes the effect of the diffusivities of both participating species and the equilibrium rate constants for the autocatalytic growth as well as those for non-linear interaction between the newly created fronts.

We also performed mean field simulations of the ordering fronts and their interactions to gain insight into our measurements on colliding OS fronts. Our simulations, which neglect the fluctuation-induced broadening of the interface identified in our previous work, show that interaction between different fronts types can give rise to asymmetry in the extent of ordering within the regions of front collision. To gain insight into this general and important phenomenon, we simulate three extreme situations within our coarse-grained autocatalytic reaction model-fronts having the same local ordering rate that simply collide and which simply exhibit competition for available space. This leads, as one might expect, to a completely symmetric extent of ordering about the center of the front collision region. We call this the symmetric front collision situation since neither front can get an upper hand over the other. We also consider the case where the presence of one ordering species inhibits the ordering of the other by its presence. In the extreme case, this front simply annihilates the other so one of the fronts simply ‘runs over’ the other. We term this the annihilating front collision and we illustrate the distorted frontal collision region that arises in this type of front collision, a situation that has some qualitative resemblance to our experimental observations on colliding OS fronts. There is another way that a species and its associated front can affect the development of a competing species front leading to a frontal collision that is asymmetric and we also consider this case for completeness. Specifically, the new species can also influence the self-interaction of a given species by its presence more that the intrinsic rate of generation (ordering) of the reference species, thereby altering the limiting extent of ordering (or steady state population in the population dynamics analog of the present problem). In this type of front collision, the front with the competitive advantage in this sense will overtake the other, but rather than exterminating the other species the fronts will come to new asymptotic coexisting steady state values of local ordering for each species, i.e., the one front and its species dominates over a recessive population. We term this type of front the coexisting front collision since the one population accommodates to the presence of the other.

We do not attempt a quantitative comparison between our reaction–diffusion model and our experiments in the present paper since the mean field theory of front evolution does not account for the fluctuation-induced front spreading, an effect that clearly must influence quantitative aspects of the frontal collision process. Nonetheless, our calculations illustrate some fundamental aspects of the front collision interaction that accounts for some of the asymmetry that we observe in our OS front collision measurements. In future work, we plan to incorporate a reasonable model of the frontal interfacial spreading so that we can more faithfully model the frontal collision process.

Acknowledgements

We thank the National Science Foundation for supporting this work through Grant no. CBET-0853667. NEXAFS spectroscopy experiments were carried out at the National Synchrotron Light Source, Brookhaven National Laboratory, which is supported by the U.S. Department of Energy, Division of Materials Sciences and Division of Chemical Sciences.

References


20 Certain commercial equipment is identified in this article in order to specify adequately the experimental procedure. In no case does such identification imply recommendation or endorsement by the National Institute of Standards and Technology, nor does it imply that the items identified are necessarily the best available for the purpose.


