Contents lists available at ScienceDirect

Computational Materials Science

An optimization approach to identify processing pathways for achieving tailored thin film morphologies

Spencer Pfeifer [a], Olga Wodo [b], Baskar Ganapathysubramanian [a,*]

[a] *Department of Mechanical Engineering, Iowa State University, Ames, IA, United States*
[b] *Materials Design and Innovation Department, University at Buffalo, SUNY, Buffalo, NY, United States*

ABSTRACT

It is well-known that the performance of thin film organic electronic devices critically depends on the active layer microstructure. Since processing conditions heavily influence the microstructure, identifying optimal fabrication conditions is a crucial step towards the development of high-performance devices. Current state-of-the-art approaches remain predominantly trial-and-error, which are time and resource intensive. In this work, we integrate a morphology evolution framework (based on a phase-field model) with a heuristic optimization scheme to systematically identify promising processing conditions. We show how annealing time and substrate patterning can be simultaneously tuned to achieve a variety of tailored microstructures. The appropriate choice of cost functional is critical to achieving meaningful results. The methodology presented here provides a scalable and extensible approach towards the rational design of tailored microstructures with enhanced functionalities.

© 2017 Elsevier B.V. All rights reserved.

1. Introduction

Modern engineering applications continue to drive the demand for heterogeneous materials with multifunctional properties [1–7]. These properties are often dependent on the microstructure and corresponding internal component configurations (atoms, phases, and compounds), which has resulted in a growing emphasis on *microstructure-sensitive design*. The intention is to identify tailored microstructures that exhibit desirable properties; or to determine the processing conditions capable of producing such morphologies. Historically, the design-to-deployment cycle for microstructure-sensitive materials has taken years to even decades to complete. More recently, however, there has been a sustained effort [8–10] to rapidly accelerate materials development by integrating effective computational tools into the design and development cycle [11,12]. The rapidly increasing power and availability of high-performance computing has facilitated the development of increasingly sophisticated computational models [10,13] that permit an exhaustive analysis of the process-microstructure-property relationships. Examples include microstructure-sensitive analysis in metals and multi-component alloys [14–17], polymer blends [18,19], and composites [20]. Consequently, such advances have opened up the possibility of coupling these 'forward' models with optimization frameworks to systematically identify promising pathways that produce microstructures with desirable properties [19,21–24].

Our focus is on a relatively newer class of microstructure design problems involving polymer blends, in which both anisotropy and confinement play a significant role in determining performance. More specifically, we are interested in the microstructure-sensitive design of polymer-based thin films (or more generally, organic thin films) for use in organic electronics. These devices generally consist of highly anisotropic, multi-component blends, with operational conditions (and hence microstructure design) that must carefully consider the impact of the film boundaries. Applications for such devices range from sustainable energy harvesting and flexible displays [25–27] to implantable healthcare diagnostic devices and sensors [28–30]. These devices are particularly attractive because they exhibit an inherent softness, flexibility, and biological compatibility – traits that are traditionally absent in conventional silicon-based systems [29]. In addition, the prospect of an inexpensive, high-speed, 'roll-to-roll' manufacturing process operating at low temperatures, makes organic thin film devices excellent candidates for 'green electronics.' However, many promising technologies are currently bottlenecked by the manufacturing stage – namely the immense challenges associated with selecting proper fabrication conditions to produce desirable morphologies with tailored properties. Addressing this shortcoming serves as the central motivation for the current work.

* Corresponding author.
 E-mail address: baskarg@iastate.edu (B. Ganapathysubramanian).
 URL: http://www.me.iastate.edu/bglab/ (B. Ganapathysubramanian).

In the sections that follow, we focus on developing an extensible and scalable optimization framework that systematically identifies viable processing conditions that result in tailored microstructures. We use the words 'microstructure' and 'morphology' interchangeably. We couple a phase-field-based morphology evolution framework [18,31,32] with a particle swarm optimization (PSO) routine. The choice of a meta-heuristic, multi-start, gradient-free optimization routine (in contrast to gradient-based methods) is made to ensure that the phase space is well-explored.

As a representative problem that illustrates this framework, we consider post-deposition annealing of an organic thin film consisting of two distinct materials (*i.e.,* a two-phase system, A-B). Post-deposition annealing (both thermal- and solvent-based) is a routinely used protocol in organic electronics to develop well-connected microstructural domains [33,34]. The annealing process encourages the progression of spinodal decomposition through coarsening behavior and results in the formation of large (A-rich phase and B-rich phase) domains. The annealing time, thus, affects the resultant final morphology. We choose the annealing time as one of the processing conditions that can be tuned to tailor the morphology. Additionally, we consider the organic thin film to be in contact with a chemically patterned substrate. The localized changes in the surface energy of the substrate (due to the chemical treatment) result in spatial variations in the way that the substrate interacts with the A-rich and B-rich domains within the thin film. Such patterning – in which the chemistry can be tuned to preferentially attract or repel one of the two components – has been shown to be very useful in modulating morphology formation [35], with dip-pen nanolithography being one successfully deployed approach [36–39]. We choose the patterning wavelength as one of the processing conditions that can be tuned to tailor the morphology. Note that the choice of these two processing variables in our illustrative example of the optimization framework also showcases the interplay between a volume-based control mechanism (annealing) with that of a surface-based control mechanism (substrate patterning). We report results for 2D domains representing the cross-sectional morphology (i.e. morphology in the direction perpendicular to the plane of the film) as the morphology variation across the depth of the thin film critically affects performance.

The outline of the rest of the paper is as follows: We provide a brief description of the phase-field methodology at the core of our morphology evolution framework in Section 2. Then, Section 3 is devoted to the development of a suitable objective function as well as implementation details of the PSO algorithm – which is developed around two processing conditions: thermal annealing and substrate patterning. Finally, Section 4 provides illustrative results from the optimization framework, followed by concluding remarks in Section 5.

2. Morphology evolution & phase-field modeling

In recent years, several groups have utilized phase-field approaches to model morphology evolution in organic thin films [18,40,41]. This class of numerical methods has become a staple mesoscale model for simulating interfacial evolution under a wide variety of physical phenomena. Such popularity is a result of the elegance with which these thermodynamically-driven models are constructed. Moreover, the 'modular' free energy-based design allows for a natural inclusion of diverse physical phenomena as well as material-specific properties – all while supporting short software development cycles [42]. In developing a coupled phase-field–PSO framework, this added versatility allows for an efficient progression from a proof-of-concept model to more realistic systems that incorporate tailoring a broader set of processing

conditions (for example, evaporation rates, spinning speeds, temperature ramps, among others).

As previously mentioned, this work explicitly focuses on a two-phase system subjected to thermal annealing in the presence of a chemically patterned substrate. The goal is to design a versatile and robust numerical framework, which is naturally extensible to broader classes of material systems and fabrication techniques.

2.1. Phase-field model

The phase-field model defines the evolution of an order parameter, $\phi(\boldsymbol{x}, t) \in [0, 1]$, which represents the local volume fraction of component A (of a binary A-B mixture), with the volume fraction of B given as $1 - \phi(x, t)$. The evolution equation is derived via formulating (and minimizing) a free energy functional that represents the energy of a given configuration of the system, $\phi(x, t)$.

Here, the free energy, F, assumes the typical Ginzburg-Landau form with an added boundary term to include substrate effects:

$$F(\phi) = \int_\Omega \left[f(\phi) + \frac{1}{2} \epsilon^2 |\nabla \phi|^2 \right] d\Omega + \int_\Gamma f_s(x, \phi) \, d\Gamma, \tag{1}$$

where Ω represents the physical domain, and Γ is limited to the lower boundary of the domain, where the system interacts with the substrate. Here, $f(\phi)$ is the local, *homogeneous* (*bulk*) free energy of mixing, which has a non-convex, double-welled profile for binary systems. For simplicity, this term is often represented by the following quartic polynomial relation:

$$f(\phi) = \frac{1}{4} \phi^2 (1 - \phi)^2. \tag{2}$$

The square gradient term in Eq. (1) represents the *interfacial* energy, and accounts for the costs associated with interface creation between two immiscible phases. The interfacial coefficient, ϵ^2, characterizes the interfacial thickness between homogeneous phases and is often correlated with the energy of forming an A-B interface, which is typically on the order of a few mJ/m^2 for organic blends. Finally, $f_s(x, \phi)$ introduces a spatially-dependent surface potential at the lower boundary to incorporate substrate patterning effects. The total energy can be described as a summation of bulk, interfacial, and surface energy contributions:

$$F = F_{bulk} + F_{int} + F_s, \tag{3}$$

which are individually tracked during morphology development, as shown in Fig. 1.

Next, the time evolution of the system is expressed by the following continuity relation:

$$\frac{\partial \phi}{\partial t} = -\nabla \cdot J. \tag{4}$$

In which the mass current, J, is related to the chemical potential ($\mu = \delta F / \delta \phi$), as follows:

$$J = -M \nabla \mu. \tag{5}$$

The species mobility, M, is assumed to be spatially uniform and independent of concentration (we set $M = 1$). Combining the above, we arrive at the Cahn-Hilliard (CH) equation:

$$\frac{\partial \phi}{\partial t} = \nabla \cdot \left[M \nabla \left(\frac{\partial f}{\partial \phi} - \epsilon^2 \nabla^2 \phi \right) \right]. \tag{6}$$

Characteristic solutions, absent of substrate effects, are provided in Fig. 1 above. Here, images (A)–(F) provide representative snapshots throughout the morphology evolution – each corresponding to a significant point along the bulk energy profile, F_{bulk}, in Fig. 1(a). More specifically, points (A) and (B) represent a disordered phase prior to bulk segregation. The short moments thereafter are characterized by a significant plunge in the bulk energy