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Formation and control of secondary nanostructures in electro-hydrodynamic patterning of ultra-thin films

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ABSTRACT

Based on a computational model involving finite element method, we report the morphological evolution and pattern formation process in a thin polymer film subject to an externally imposed periodically varying heterogeneous DC electric field, induced by topographically patterned top electrode. Quasi-steady state morphology is observed to depend on remnant liquid layer after the evolution of primary structures. The dynamics of remnant layer de-wetting that essentially is dictated by electrode assembly, fluid properties, and initial film thickness, results in formation of intermediate secondary structures. The possibility of controlling these structures is explored by varying periodicity of the stamp/top electrode, applied potential and initial liquid volume. At a fixed operating condition, critical periodicity is identified for stable secondary structure formation that may lead to ordered nano-patterns for diverse applications.

1. Introduction

Polymer films and surfaces with meso- and nano-scale topographic patterns find wide applications in many technologically important areas such as nanobiotechnology [1], microfluidic mixing [2], lab-on-a-chip devices [3], hydrophobic and self-cleaning surfaces [4], bulk heterojunction solar cells [5,6], organic light emitting diodes [7], etc. While top down lithography based techniques are widely used for nano-patterning [8], various alternative approaches exploiting the spontaneous and external field mediated instability are gaining popularity, particularly in terms of unprecedented flexibility in morphology control [9]. In this context, electro-hydrodynamic (EHD) instability is of particular interest where a thin film sandwiched between two electrodes is destabilized by the application of an external electric field [10]. An externally imposed electric field can destabilize a much thicker film because of its higher strength and long range nature of electrostatic interactions whereas spontaneous instabilities engendered by dispersion forces (e.g., de-wetting of a thin film) are manifested only in films thinner than 100 nm [11]. While the influence of an electric field on the surface of a viscous film was reported by Swan [12] as early as 1897, the concept of using EHD instabilities for nano-patterning of a polymer thin film was first demonstrated by Schäffer et al. [10] as late as 2000.

In EHD instability, an electric field across the polymer film–electrode assembly (Fig. 1) imposes a force that is normal to polymer-bounding fluid interface. This electrical force triggers the growth of surface fluctuations overcoming the stabilizing influence of surface tension, so as to minimize the total electrostatic potential energy. The interplay of interfacial tension and electrostatic forces characterize a wavelength (λ_c) of the growing instability which dictates the final morphology of the spatiotemporal evolution. However, this final morphology of polymeric pillars is a quasi-steady state which on prolonged exposure of the electric field, starts to coalesce. Therefore, the desired structures are required to be cured in time. EHD instability with a flat top electrode (Fig. 1a) results in random pillars where the λ_c is determined based on initial film thickness, field strength and the gap between the electrode and thin film. In such scenario, λ_c is estimated through linear stability analysis, [10,13,14] which has a functional form:

$$\lambda_c = 2\pi\sqrt{\frac{2\gamma\psi}{\epsilon_0\epsilon_p(\epsilon_p-1)^2}}E_p^{-3/2} \quad (1)$$

where γ, ψ, ϵ_0, and ϵ_p are interfacial tension, applied voltage, permittivity of free space, and relative permittivity of polymer film to the bounding fluid, respectively. Furthermore, E_p, the electric field at the film–bounding fluid interface is defined as,

$$E_p = \frac{\psi}{\epsilon_p d-(\epsilon_p-1)h} \quad (2)$$

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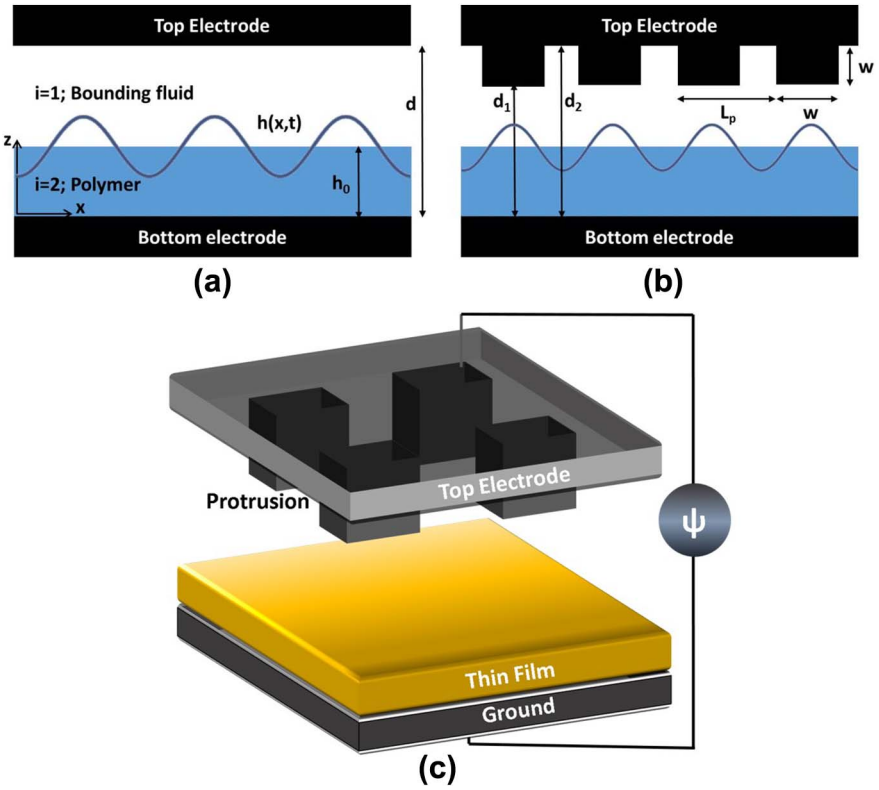

Fig. 1. Schematic of electrode assembly with polymeric liquid film denoting the geometrical parameters and top electrode as (a) flat plate, (b) patterned stamp with square protrusions, and (c) 3-D representation of patterned stamp electrode assembly.

Typically, the lateral dimension of patterns in electric field induced patterning is limited by the value of λ_c [10,15,16]. Additional ordering of instability patterns as well as miniaturization has been achieved by using a topographically patterned top electrode [9,10,17](Fig. 1b and c). Such a system induces laterally varying electric field and controls the final morphology by directing the growth of instability towards the top electrode protrusions, which results in structures at the length scale of each electrode features.

The dynamics of spatiotemporal evolution as well as final morphology of patterns in EHD instability systems with patterned top electrode owe its sensitivity towards several parameters such as initial film thickness (h_0), gap spacing (d), pattern periodicity (L_p), and geometry of electrode. Several numerical studies have been reported to understand various aspects of EHD instability, including the pioneering work of Sharma and co-workers [17], who showed the influence of top electrode geometry on the formation of polymeric patterns. Harkema et al. [18] explained the mechanism of pattern formation through experimental observations by categorizing regimes of morphologies with the variation in stamp periodicity (L_p). Russel and co-workers [16,19] studied the shape of polymeric structure arrays using non-linear simulations. Theoretical understanding of EHD instability has also been delineated for polymer bilayers [20] and trilayers [21]. Bandyopadhyay et al. [22] presented the analysis of non-Newtonian dynamics under the influence of electric field. The effect of electrostatic heterogeneity is numerically investigated in thin ionic liquid films [23,24]. The effect of chemical heterogeneity on the EHD pattern formation along with other system parameters was previously addressed by one of us [25]. Goldberg-Oppenheimer and Steiner pioneered the application of EHD instability as a viable technique for patterning of various functional materials such as conductive polymers [26], block co-polymers with hierarchical orientation control [27], crystalline polymer [28] etc. including possible creation of hierarchical structures, which have been used for surface-enhanced Raman scattering [29]. They also showed the possible use of EHD instability in aligning carbon nanotubes [30], which has been utilized for creation of surface patterns with tunable wettability and adhesion [31]. Recent simulation studies report various numerical schemes [32,33] along with lesser computational efforts using finite element [34,35] and boundary element [36] methods. Additionally, variety of structures that can be formed using EHD induced patterning are elaborated in numerous numerical and experimental studies [37–43].

It is well understood that even when varying a patterned top electrode, nano patterns can be replicated on the polymeric film at the length scale of each electrode feature only within a narrow and specific parameter window [9,15,17,35]. While studying the influence of electrode geometry on polymeric patterns at larger L_p ($\gg \lambda_c$ for heterogeneous field), Verma et al. [17] reported the formation of secondary structures. These structures increase density of polymeric patterns over the domain, although the pattern periodicity of the top electrode remained constant. The rise of secondary patterns was linked with capillary wave which was generated by the disturbance created during the rise of primary patterns [18]. Harkema et al. [18] also described a general case where a single protrusion gave rise to capillary waves that triggered the growth of secondary patterns. However, the present work deals with confined capillary dynamics within a series of protrusions. Interestingly, no systematic investigation that captures the dynamics at the critical L_p is present in open literature. Contextually, this study addresses morphological changes that a polymeric film undergoes when subjected to a patterned top electrode with large L_p. We analyze the formation of secondary structure morphology, that evolves from the remnant fluid layer after the growth of primary structures. We primarily focus on the dynamics of this remnant layer that governs the morphology of secondary patterns. Limiting conditions for the formation of these structures are methodically explored. We show that based on an interplay of top electrode pattern periodicity (L_p), initial thickness of polymeric film (h_0) and the applied voltage (ψ), an assortment of ordered nanostructures can be achieved.