Controlled Nanoscale Electrohydrodynamic Patterning Using Mesopatterned Template

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ABSTRACT: We report the path for a possible fabrication of an array of nanogrooves, by electro-hydrodynamic instability-mediated patterning of a thin polymer film using a patterned stamp with much larger features. Using a predictive computational model based on finite element method, we find the route to control the coalescence of initial instabilities that arise with the onset of spatially varying DC electric field generated through topographical patterns in the top electrode. These quasi-steady structures are shown to evolve with the electrostatic and geometric nature of the two-electrode system and are of a stable intermediate during the process of feature replication, under each electrode feature. We identify conditions to obtain nanogrooves for a range of operating conditions. Such simulations are likely to guide experiments, where simultaneous optimization of multiple parameters to fabricate features with lateral dimension smaller than that of the electrode patterns is challenging.

1. INTRODUCTION

In a time when miniaturization is the need of hour, rapid and effective techniques of synthesizing nano/mesoscale patterns are in high demand. These structures are used in various fields of nanobiotechnology,† lab-on-a-chip devices,‡ microfluidics,§ hydrophobic and self-cleaning surfaces,¶ bulk heterojunction solar cells,¶,∥ organic light-emitting diodes,¶ and so on. Consequently, researchers have turned to various novel patterning techniques to engineer surfaces and structures that are not easily manufactured by conventional top-down lithographic methods.¶ However, lithographic techniques are generically expensive, meticulous, and often has limitations either in terms of throughput or resolution.¶ Recently, spontaneous instability-mediated morphological evolution in ultrathin films, particularly in conjugation with lateral confinement, is being considered as a viable nonlithographic mesofabrication technique for soft materials.¶ Such instabilities result because of applications of thermally excited capillary waves engendered by van der Waals force-mediated disjoining pressure and are thus limited only in ultrathin films (h ≤ 100 nm). On the other hand, much thicker films can be destabilized by the action of an externally applied field, such as an electric field or a thermal gradient. Although the stability and dynamics of fluid−fluid interfaces subject to an externally applied electric field was studied first by Swan in 1897, it was only around the year 2000 when Schäffer et al.‡ pioneered the concept of electric-field-mediated instability for patterning thin polymer films, which has been termed as electrohydrodynamic (EHD) lithography. EHD instability-mediated patterning, which uses a capacitor system with thin/ultrathin films of polymers, provides excellent ability of morphology control, in comparison with direct embossing-based techniques.¶,∥,‡,‡,‡ Apart from thin films of homopolymers, films of various functional materials such as conductive polymers, block copolymers, inorganic thin films, and so on have been patterned by EHD instability.¶,∥,∥,∥ Fabrication of high aspect ratio structures was accomplished by Lv et al.‡,‡,‡ in their recent studies. The destabilizing effect of electric forces on the free surface of a thin film has been well-explored by numerous researchers.‡,‡,‡,‡,‡,‡,‡,‡,‡,‡ A significant advantage of using EHD is the accomplishment of control over the length scale of the surface patterns.¶,∥,∥,∥ However, required external source of energy, breakdown of dielectric polymer at high voltages, and involvement of several influencing parameters are challenges to this technology.¶,∥ Schäffer et al.‡ found that careful control of EHD instabilities can be exploited to generate well-defined pillars because they could replicate a patterned top electrode on a sub-micrometer lateral dimension. Various experimental observations with a flat top and bottom electrode show the evolution of isotropic structures with a dominant wavelength that corresponds to the fastest growing mode of instability, which governs the spatiotemporal evolution and the final morphology of the features. Theoretically, an expression for the fastest growing mode of instability can be obtained.
from a linear stability analysis, the expression for which is

\[ \lambda_c = \frac{2\pi}{\sqrt{\frac{2\gamma \psi}{\varepsilon_0 \varepsilon_p (\varepsilon_p - 1)^2} E_p^{-3/2}}} \]  

where \( \gamma \), \( \psi \), \( \varepsilon_0 \), \( \varepsilon_p \), and \( E_p \) are interfacial tension, applied voltage, permittivity of free space, relative permittivity of polymer film to the bounding fluid, and electric field intensity at the polymer–air interface, respectively.

It can be seen that the characteristic wavelength is a function of both the geometry and electrostatic parameters of the system, which is an interplay between the electrostatic and surface tension forces. Additional control and ordering of the instability features including possible miniaturization can be achieved by using a topographically patterned top electrode, where patterns are seen to replicate below each protrusion of the patterned top electrode. Under a patterned top electrode, the gradient in electric field strength because of the presence of heterogeneity strongly influences the evolution process, and consequently the pattern periodicity \( (L_p) \) and geometry of the top electrode determine the final morphology, in addition to initial film thickness \( (h_0) \), gap spacing \( (d) \), and field strength. Several theoretical and numerical studies have been carried out to mathematically elucidate the patterning process as well as to identify the conditions for the formation of ordered patterns on single and/or multilayer thin films. With a nonlinear 3D model for polymer/substrate morphology, Verma et al. identified the ideal conditions necessary for pattern replication and indicated that the number density of the replicated patterns can be altered by varying the applied voltage or tuning the mean film thickness, periodicity, and depth of grooves on the top electrode. Moreover, they predicted the possible formation of secondary structures between two parallel ridges, which was also experimentally substantiated by Harkema. The formation of secondary structures has been related to the depletion of liquid during the formation of primary continuous ridges. Atta et al. showed the self-assembly of ordered nanopillars on the introduction of marginal chemical heterogeneity on the surface of electrode assembly. Electrically heterogeneous patterned electrodes have also been used for the fabrication of re-entrant structures which are beyond the fabrication capability of imprint lithography. Recently, researchers have also investigated EHD patterning of prepatterned surfaces in search of novel and miniaturized structures.

On the basis of a careful review of published literature, we identify that there is no clear study that elaborates the morphological evolution of stable intermediate structures, particularly capturing the transition of single to multiple pillars under a solitary protrusion of the top electrode. In this study, we report an intermediate structure in case of an insufficient peak splitting during the transitional regime from single to multiple pillars under one protrusion that results in a toothlike cavity, termed as nanogroove. We identify the relation between width of the protrusion \( (w) \) and \( \lambda_c \), as the effect of \( L_p \) on \( \lambda_c \) is already well-perceived. A numerical model based on finite element method is employed to investigate the influence of filling factor, initial film thickness, applied voltage, protrusion height, and electrode spacing on the obtained quasi-steady-state patterns. These results are of paramount importance in designing, optimization, and fabrication of ordered nanostructures, which particularly will be able to guide toward the desired morphology avoiding undesired coalescence of patterns. Fabrication of such nanoscale structures using a stamp with a much larger lateral dimension is the key novelty of this work, particularly from the standpoint of nano-fabrication.
2. MATHEMATICAL FORMULATION

2.1. System Description. Figure 1 shows the schematic of the EHD assembly, where the bottom electrode is coated with ultrathin polymeric film of initial thickness of \( h_0 \) and the confined space above the film is occupied by air as the bounding fluid. The electrode assembly with variable \( d(x) \) because of protrusion at the top electrode results in heterogeneous electric field, where as the flat plate assembly produces homogeneous electric field in lateral direction. Along with gap spacing \( (d) \), other parameters that define a heterogeneous system, such as electrode width \( (w) \), pattern height \( (p) \), and stamp periodicity \( (L_p) \) are depicted in Figure 1b. Figure 1c represents a 3D structure of the physical system with columnlike top-electrode protrusions. The interfacial perturbation with the onset of electric field by applying a DC potential of \( \psi \) at the top electrode and keeping the bottom as ground results in film thickness \( h(x,t) \) as a function in space and time domain. This thin-film system is considered to be isothermal, incompressible \( (\rho = 1000 \text{ kg/m}^3) \), Newtonian \( (\mu = 1 \text{ Pa}\cdot\text{s}) \), and perfect dielectric \( (\epsilon_e = 2.5) \) with air–polymer interfacial tension \( (\gamma) \) as 0.038 N/m.

2.2. Governing Equations and Boundary Conditions.

2.2.1. Fluid Flow. The governing equation for this incompressible Newtonian fluid is defined by the set of Navier–Stokes (eq 2) and continuity equation (eq 3), coupled with Maxwell equations to account for the presence of external electric field.

\[
\rho \left[ \frac{\partial \vec{u}}{\partial t} + (\vec{u} \cdot \nabla) \vec{u} \right] = -\nabla P + \nabla \left[ \mu (\nabla \vec{u} + (\nabla \vec{u})^T) \right] + \vec{f}
\]

\[
\nabla \cdot (\vec{u}) = 0
\]

where \( f \) represents the body forces and the subscript denotes the phases \( (1 \text{ for air and } 2 \text{ for polymeric film}) \).

2.2.2. Boundary Conditions. At the upper and lower electrodes, no slip boundary conditions are applied.

\[
\vec{u}_i = 0 \text{ at } z = 0 \quad \text{and} \quad \vec{u}_i = 0 \text{ at } z = d_{1,2}
\]

At the interface, continuity of velocity is assumed.

\[
\vec{u}_i = \vec{u}_j \text{ at } z = h(x, t)
\]

The interfacial velocity \( (\omega) \) under an infinitesimal perturbation is related to the film thickness by the following kinematic boundary condition.

\[
\omega = \frac{\partial h}{\partial t} + u \frac{\partial h}{\partial x} \text{ at } z = h(x, t)
\]

To simplify and solve the governing equations for this system, we assume \( (a) \) two fluids as immiscible with no interphase mass transfer across the interface, \( (b) \) the film is sufficiently thick that continuum assumption is valid but thin enough so that the effect of gravity can be neglected, and \( (c) \) inertial effects will be negligible because of ultrathin film condition. These simplifications along with the consideration of long-wave approximation\(^6^0\) give rise to the temporal evolution of thin-film height that can be described by the following expression

\[
\frac{\partial h}{\partial t} = \frac{\partial}{\partial x} \left[ \frac{h^3}{3 \mu} \frac{\partial \psi}{\partial x} \right]
\]

where

\[
\psi = \psi_0 - \frac{\partial^2 h}{\partial x^2} + \psi_{el} + \psi_{LW}
\]

In eq 8, \( \psi_0, \psi_{el} \) and \( \psi_{LW} \) represent atmospheric pressure, electrostatic pressure, and disjoining pressure because of Lifshitz–van der Walls (LW) interactions, respectively. Moreover, \( \psi_{el} \) and \( \psi_{LW} \) can be estimated from the following equations\(^3^6,5^5\)

\[
\psi_{el} = -\frac{1}{2} \sigma \epsilon_e \epsilon_p (\epsilon_p - 1) E_p^2
\]

\[
\psi_{LW} = \frac{A_L}{6 \pi h^3}
\]

where \( A_L \) is the effective Hamaker constant for interactions between the free surface of the film and lower solid surface through the fluid film. In our case, \( \psi_{LW} \) can be neglected because of the presence of dominant electrostatic force. Detailed derivation of the aforementioned equations can be found elsewhere.\(^3^6,3^8,5^2,5^5\)

3. COMPUTATIONAL MODEL

As shown in Figure 2, a 2D model in COMSOL Multiphysics\(^6^2\) has been developed to realize the evolution of the structure because of the electrostatic force and surface tension at the interface of the liquid polymer. The 2D computational model exemplifies columnlike physical system, as shown in Figure 1c in three dimensions. DC potential is implemented between the bottom (boundary 2) and the top electrode (boundaries 5–21). Other boundary conditions for the solution are \( (a) \) no slip at boundaries 2, and 5–21; \( (b) \) symmetry on boundaries 1, 3, 22, and 23; \( (c) \) initial fluid interface at boundary 4; and \( (d) \) pressure point constraint at points a and b, which are the two ends of the air film interface. The polymer–air interface is tracked by using conservative form of the level-set method (eq 11),\(^6^2\) where a phase is characterized by a level-set function \( \phi_{\text{lr}} \) which is 0 in case of air and is 1 for polymer. Consequently, the interface is captured by contour of level function \( \phi_{ls} = 0.5 \).

\[
\frac{\partial \phi_{ls}}{\partial t} + \nabla \cdot (\vec{u} \phi_{ls}) = \gamma \nabla \cdot \left( \epsilon_e \nabla \phi_{ls} - \phi_{ls} (1 - \phi_{ls}) \frac{\nabla \phi_{ls}}{\sqrt{\nabla \phi_{ls}^2}} \right)
\]
where \( \gamma_h \) determines the amount of reinitialization of the level-set function and the parameter \( \epsilon_{ls} \) specifies thickness of the interface. A suitable value for \( \gamma_h \) (0.1) is the maximum magnitude of the velocity field in the model, and \( \epsilon_{ls} = h_t/2 \), where \( h_t \) is the maximum element size across the interface.

Furthermore, the assumptions of film and air as perfect dielectric media with zero net charge in the bulk results in equations governing the force exerted on the interface. This is resolved using the following Laplace equation.

\[
\nabla \cdot (\epsilon_0 \epsilon \nabla \psi) = 0
\]  

(12)

where \( \epsilon_0 \) is the dielectric permittivity of the vacuum, \( \psi \) is the voltage, and \( \epsilon_t \) is the dielectric constant of the air or polymer, defined as \( \epsilon_t = 1 + 1.5 \phi_{ls} \). The level-set function smooths the material property such as density, viscosity, and dielectric constant jump across the interface as follows:

\[
\rho_i = \rho_1 + (\rho_2 - \rho_1)\phi_{ls}
\]  

(13)

\[
\mu_i = \mu_1 + (\mu_2 - \mu_1)\phi_{ls}
\]  

(14)

\[
\epsilon_t = \epsilon_1 + (\epsilon_2 - \epsilon_1)\phi_{ls}
\]  

(15)

The body-force term in eq 2 is implemented as follows

\[
\mathbf{f}_i = (E_{el} + E_{st})
\]  

(16)

Two components of the body-force term \( f_i \) in eq 16 are volumetric forces because of surface tension, \( F_{st} = \gamma \delta n \), and electrostatic force, \( F_{el} = p_d \delta n \), where the electrostatic pressure \( p_d \) is a simple Dirac delta function that is concentrated at the interface and in level set method, and \( \delta = 6\phi_{ls}(1 - \phi_{ls})||\nabla \phi_{ls}|| \) provides a smooth transition along the interface. \( \mathbf{n} \) is the unit outward normal to the interface, and \( \kappa \) is surface curvature estimated as: \( \kappa = \nabla \cdot \mathbf{n} \).

4. RESULTS AND DISCUSSION

In case of a homogeneous electric field, EHD-induced patterning is analytically described by characteristic wavelength derived from linear stability analysis of the system. In a system of two flat electrodes (Figure 1a), the gradient of electric pressure at extreme corners is responsible for the initial perturbation of interface, which consequently propagates creating a pressure gradient along the interface. This mechanism is essentially responsible for the formation of nanopatterns in case of a flat electrode assembly. However, in case of a topographically patterned top electrode (Figure 1b), difference in electrical pressure is locally generated over the interface at the level of each feature on the top electrode, and this variation subsequently triggers a secondary instability is detected, which rises because of the ripple created by the gradient of electric pressure. For complex systems with patterned top electrode, there is no single characteristic \( \lambda \) owing to varying gap spacing. In such systems, on moving from bottom electrode to the top, we find two gap spacings, \( d_1 \) and \( d_2 \), which are minimum and maximum separation distances between top and bottom electrodes. Characteristic wavelength of instability corresponding to \( d_1 \) and \( d_2 \) are denoted by \( \lambda_{d_1} \) and \( \lambda_{d_2} \), respectively. From a number of simulations, it is evident that secondary instability is first observed in between \( \lambda_{d_1} \) and \( \lambda_{d_2} \), where two separate pillars form under one protrusion, and this leads to a novel and intriguing morphological structure having nanogrooves on the top. In such cases, ripple created by the inflow gradient tries to rip the rising pillar, although it is not strong enough to snap completely. These structures attain quasi-steady state as confirmed by the simulations in our study. In an attempt to estimate this morphological transition and its relation to influencing parameters, we have identified five different electrode widths that are on the basis of characteristic \( \lambda \) (eq 1), as: \( \lambda_{d_1} \), \( \lambda_{d_2} \), \( \lambda_{d_2', \lambda_{avg}, \lambda_{d_2}} \), and \( \lambda_{d_1} \) for electrode spacing (\( d \)) as \( d_1 \), \( (d_1 + d_{avg})/2 \), \( d_{avg} \), \( (d_{avg} + d_2)/2 \), and \( d_2 \), respectively, where \( d_{avg} = (d_1 + d_2)/2 \).

4.1. Mechanism of Structural Evolution. Understanding of structural evolution in case of transitional structure not only provides better understanding about the evolution process but also reveals the key parameters that control the transition from single to multiple pillars under one protrusion. Although the flow of polymer is a function of instantaneous electric field distribution, it can be shown that initial electric field distribution can be a fair metric for predicting the final morphology, and the subsequent dynamics. Maximum \( (E_{max}) \) and minimum \( (E_{min}) \) field strengths across the interface are just beneath the center of protrusion and the groove of top electrode, respectively (Figure 3). The inflow gradient drives the fluid from outside toward protrusion and is proportional to \( (E_{max} - E_{min}) \) across the interface.

![Figure 3](image-url)  

Figure 3. Initial electric field intensity distribution on a 30 nm polymeric film under protruded top electrode having \( w = \lambda_{d_1} = 214 \text{ nm}, \) and \( p = 20 \text{ nm} \) for 70 V, \( d_1 = 100 \text{ nm}, \) and \( L_p = 350 \text{ nm}. \)

Figure 4 demonstrates the progressive evolution of a 30 nm liquid film under the applied DC potential of 70 V using a 214 nm \( (\lambda_{d_1}) \times 20 \text{ nm} \) protruded top electrode and gap spacing \( (d_2) \) of 100 nm. Instabilities can be seen rising from the edges because of the presence of the inflow gradient, which pulls polymeric fluid from outside of the protrusion inward at the
edges, as shown in Figure 4b. Thereafter, these instabilities derive the polymeric fluid toward the center of the protrusion in the horizontal direction and vertically upward because of the electrostatic pressure (Figure 4c). Although inflow gradient drives the fluid toward the spatial region beneath the protrusions, incoming fluid does not get equally distributed in the whole region creating two bulges, similar to what is observed under a flat top electrode as is evident from Figure 4c. This growth attains a quasi-steady state, when the rising front of a growing pillar touches the top electrode (Figure 4d) and subsequently remains unaltered (Figure 4e).

4.2. Influence of Filling Factor. The filling factor, defined as the ratio of \( w/L_p \), is a key parameter in systems with topographically patterned top electrode that limits the patterning range. Its effect on the final morphology can be observed by either changing \( w \) or \( L_p \) at a time. Figure 5 shows the variation in the final morphology when \( w \) is varied from \( \lambda_{d_e} \) to \( \lambda_{d_t} \) keeping \( \psi = 70 \text{ V}, \ h_0 = 30 \text{ nm}, \ L_p = 350 \text{ nm}, \ d_2 = 100 \text{ nm}, \) and \( p = 20 \text{ nm} \). It is evident from Figure 5a that single pillar is observed when the width of top electrode is 210 nm (<\( \lambda_{d_e} \)). Further increase in the width of protrusion, a pillar with nanogroove is observed at \( w = \lambda_{d_t} = 214 \text{ nm} \) (Figure 5b), and for \( w = \lambda_{d_t} = 214 \text{ nm}\) the grooves become deeper that touch the ground electrode (Figure 5c). Two distinct pillars are observed at \( \lambda_{d_{eq}} \) (Figure 5d), and further increase in \( w \) results in even more distant pillars under one protrusion at \( w = \lambda_{d_0} \) (Figure 5f).

This development is consistent with our observations of initial electric-field-intensity distribution (Figure 6), where it is apparent that the gradient of electric field is maximum at the corners of the protrusion and vanishes on approaching the center. The region of low-electric-field gradient increases with an increase in protrusion width (\( w \)). Therefore, the final morphology is seen to shift from a high degree of coalescence (single pillar) to partial coalescence (nanogroove structures) to no coalescence (multiple pillars) (Figure 5). The parameters are selected in such a way that periodicity value is sufficiently larger than the electrode width. For comparable values, one may encounter two major issues. First, fabricating within tens of nanometers with accuracy is a problem, and second, the system will start behaving similar to a flat plate because of very small distance between two protrusions. The gap region with low electric field strength will be negligible compared to area under protrusion, and results similar to a flat plate might be obtained. Figure 7 demonstrates the filling factor variation by changing the pattern periodicity \( L_p \) from 250 to 400 nm, keeping voltage at 70 V, film thickness \( h_0 = 30 \text{ nm}, \) electrode spacing \( (d_2) = 100 \text{ nm}, \) and pattern height \( (p) \) at 20 nm. At a fixed electrode width \( w, \) the inflow gradient increases with \( L_p \) and the system shows higher degree of deviation from a flat electrode system (Figure 8). It can be understood that at higher \( L_p \) values, formation of multiple pillar is more favorable as compared to single pillar because of enhanced flow of material resulting from high inflow gradient, which alleviates the nanogroove formation. Therefore, it is worth noting that we show fabrication of structures that are much smaller than features on the stamp,
other parameters. We observed a single pillar under the protrusion in case of $h_0 = 25$ nm (Figure 10a), which is in line with our expectation as $w = 225$ nm < $\lambda_{d_1} = 229$ nm (Figure 11). In case of $h_0 = 30$ nm (Figure 10b), the nanogroove structure is observed as $\lambda_{d_2} = 213$ nm < $w = 225$ nm < $\lambda_{d_3} = 240$ nm. Similarly, we noticed separated polymeric pillars when $h_0 = 35$ nm (Figure 10c) as $\lambda_{d_3} = 225$ nm. Thereafter, pillar separation increases in case of 40 nm thick polymeric film (Figure 10d) as $w = 225$ nm > $\lambda_{d_3} = 208$ nm. Figure 11 shows the characteristic $\lambda$ defined for different film thicknesses and summarizes the results obtained through identification of three zones where single, nanogroove, and separate pillars are more likely to be observed.

4.4. Influence of Electric Potential. Quasi-steady-state structures of 30 nm polymeric film at varying electric potential for a fixed $L_p$ and $h_0$ is shown in Figure 12. At higher potential, the inflow gradient increases and with increasing voltage, the likelihood of formation of nanoscale groove increases. For example, at 60 V, $L_p = 350$ and 30 nm initial film thickness, nanogrooved structure is not observed, but it becomes prevalent with increasing the electric potential to 70 V keeping the other parameter fixed. It should be noted that there is an upper limit of applied voltage for a particular system above
which the dielectric breakdown point of polymer has to be taken into account.

4.5. Influence of Protrusion Height and Electrode Spacing. An increase in protrusion height \((p)\) effectively reduces the gap between the top electrode and the interface, which increases the perturbing force. Accordingly, the characteristic wavelength values decrease while the ease of groove formation is enhanced. In Figure 13a, the formation of a single pillar is observed when the protrusion height \((p)\) is 10 nm with \(\psi = 70\ V\), \(w = 214\ nm\), \(d_2 = 100\ nm\), and \(L_p = 350\ nm\). By keeping all other operating parameters fixed, we observed the nanogroove structures when \(p\) was increased to 20 nm (Figure 13b). Two separate pillars are detected at \(p = 30\) and 40 nm (Figure 13c,d). On the contrary, with increasing electrode spacing \((d)\), exactly opposing behavior is found as the electrode-film interface gap increases with increasing \(d_2\) and the formation of nanogrooved structures becomes more difficult (Figure 14).

5. CONCLUSIONS

In this article, a 2D computational model based on finite element method has been utilized to study the thin film dynamics under the action of an external electric field in the presence of a topographically patterned top electrode. It is shown that by applying a heterogeneous electric field, nanogrooved structures can be produced through controlled ripple formation at the fluid–air interface. Under topographically patterned top electrode having width corresponding to \(\lambda_c\), spatiotemporal variation of the morphological patterns beneath a single protrusion is reported. Effect of filling factor, applied voltage, initial film thickness, protrusion height, and electrode spacing on the formation of structures are systematically characterized. The study is significant in elucidating the sensitivity of several independent parameters such as \(\lambda_c\), \(L_{eo}\), \(h_0\), and \(\psi\) on EHD instability in a thin polymeric film. Systematic investigation indicates \(\lambda_{d_2} < w < \lambda_{(d_2+h_0)/2}\) as a first approximation for nanogroove structures, and this study can further be used to optimize the process parameters for desired morphology. It also suggests a recipe for miniaturization with desired nanostructures under appropriate
condition in the form of possible fabrication of nanogrooves starting from a patterned stamp with a much wider lateral dimension. Such miniaturization of feature dimension is not possible in any of the direct embossing-based patterning techniques.

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**Notes**  
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