

**Main Manuscript for**

**Sublimation of Isolated Toric Focal Conic Domain on Micro-Patterned Surfaces**

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Figures 1 to 5

**Abstract**

Toric Focal Conic Domains (TFCDs) in smectic liquid crystals exhibit distinct topological characteristics, featuring torus-shaped molecular alignment patterns with rotational symmetry around a central core. TFCDs have attracted much interest due to their unique topological structures and properties, enabling not only fundamental studies but also potential applications in liquid crystal (LC)-based devices. Here, we investigated the precise spatial control of TFCDs arrangement using micropatterns and sublimation of TFCDs to estimate the energy states of the torus-like structures. Through simulations, we observed that the arrangement of TFCDs strongly depends on the shape of the topographies of underlying substrates. To accurately estimate the energetic effects of non-zero eccentricity and evaluate their thermodynamic stability, we propose a geometric model. Our findings provide valuable insights into the behavior of smectic LCs, offering opportunities for developing novel LC-based devices with precise control over their topological properties.

**Significance Statement**

While molecular evaporation of a material in an isotropic phase is naturally observed, evaporation in an ordered state, i.e. sublimation, occurs in relatively few materials. Furthermore, molecular sublimation in the liquid crystal phase remains highly uncommon. Our research has uncovered a structural evolution of an independent toroidal structure made of the smectic liquid crystal during its thermal sublimation process. Additionally, we adopted a geometric model that comprehensively describes the process by calculating the energy effect at non-zero eccentricities. This research not only unveils the coexistence of smectic liquid crystal formation and sublimation within a single substance through controlled spatial manipulation but also offers a theoretical analysis to elucidate their curvature-dependent behavior.

**Introduction**

Self-assembled structures, defined as shaping and forming ordered patterns, represent a fundamental concern across natural sciences in general, and particularly within the field of soft matter physics.(1-5) Particularly notable instances of the intricate relationship between the molecular organization of soft material and resultant order and orientation are evident in various morphologies. Among complex structures of soft materials, the layered smectic structures featured by a pseudo-one-dimensional periodic arrangement of molecules are influenced by factors like layer spacing and the delicate balance between the elastic energy of soft materials and the interfacial affected of surroundings. Examples of such soft material systems include block copolymers,(6, 7) stacked membranes,(8-10) and various liquid crystals (LCs).(11-16) LC is a state of matter with intermediate properties between liquids and crystals. Of particular interest is the smectic phase of LC, characterized by its layered molecular ordering, in which the molecules are arranged in layers that preserve their equidistance.(17-22) Structures in the smectic A phase are characterized by the ordered arrangement of molecules normal to a layer, with long-range positional order within the layers but only short-range positional order between the layers.(23-26) One of the structural features in the smectic A phase is the dimple-like defects, so-called toric focal conic domains (TFCDs).(15, 26-29) Due to the high elastic energy at the line defects around the core part of TFCDs, it is preferred to release the energy by rearrangement of local directors near the line defects when the sample is perturbed. For example, when guest materials such as colloidal particles(13, 30) and reactive mesogens (31, 32) are introduced to TFCDs, they are trapped in the defect core. Furthermore, by manipulating the physically constrained space where TFCDs form, it is possible to control the hexagonal lattice arrangement of TFCDs and their density and arrangement to be balanced between the elastic energy and the surface anchoring energy at the boundaries.(27, 28, 33)

Recent studies show the intriguing results that sublimation of semi-fluorinated molecules in TFCDs at the smectic LC phase leads to the evolution of the layering morphologies at micro- and nano-scales through leaving and re-condensing of the molecules from the surface, which is quite different from the previous researches focused on manipulating the arrangement of TFCDs or utilizing the structure of TFCDs.(11, 15, 30, 34) Sublimation occurs from the LC surface structure while maintaining the internal layered structure, which is strongly influenced by the presence of semi-fluoroalkyl chains due to the specific charge balance.(35, 36) Despite the precise control achievable over the arrangements of TFCDs through the utilization of topographic patterns and applied electric fields,(37, 38) the investigation of TFCD sublimation has been limited to closely packed hexagonal arrays.(11, 15) In this study, we observe the sublimated smectic LC layers of the isolated TFCD to provide a better understanding the intricate interplay with elastic energy and surface anchoring. For this, various micro-patterned silicon substrates are utilized, including channels, circles, and ellipses, in which the diverse morphologies of TFCDs are investigated rather than the conventional hexagonal arrangement. Various shaped TFCDs exhibit distinct thermally evolved structures via the sublimation and re-condensation process, depending on the shape of the patterned substrates. The experimental results obtained from direct observations match to theoretical analysis in elucidating the morphogenesis of sublimated TFCDs across a wide range of topographical shapes. We believe the presented results can give a hint to realizing a new soft matter design concept that utilizes sublimation and condensation to deliberately deform and pattern unexplored structures.

**Results**

**Sublimed morphologies of smectic TFCD**

Fig. 1a illustrates the chemical structure and phase transition temperatures of Y002, a synthesized molecule with a perfluoroalkyl chain added to achieve its sublimation. Its unique properties have been studied in earlier researches.(11, 15, 34) Y002 becomes an isotropic liquid state at temperatures above approximately 190 °C, and a smectic A phase between 114 °C and 190 °C without passing through the nematic phase. In this phase, the molecules of a LC are arranged in layers or sheets that are parallel to one another. The layers are typically spaced apart by a distance that is roughly the same as the length of the LC molecule.(24, 39-41) Within the smectic A phase, a particular type of structure called the TFCD can arise. TFCDs are created in a smectic A phase when the LC molecules are placed between conflicting anchoring boundaries where one prefers planar anchoring and the other prefers homeotropic anchoring. As a result, the smectic layers seek to form a tangentially bent layer-stacking from one boundary to the other, forming a toroidal domain with a surface-frustrated singularity, in which director of LC molecules are unable to be defined in three dimensions. The toroidal domains are closely packed and all connected with layering and a local director field in each domain forms two types of topological defects, one is line defect at the core of TFCD and the other is a circular defect at the bottom, schematically represented in Fig. S2a.(42-44) The smectic layers are illustrated with pink color on the left side of the image in fig. 1c, with a noticeable indentation, called "dimple", located at the center of the TFCD domain (see also the hexagonal arrays of dimples in Fig. S2b, S2c). The arrangement of TFCDs is typically hexagonal when deposited on a flat substrate; however, TFCDs exhibit different arrangement depending on geometries of underlying substrates, such as channel and micro-posts.(28, 44-46) Arrays of TFCDs can be affected with a complex interplay between the elastic energy caused by the curvature of the LC layer and the surface energies of the air-LC and substrate-LC interfaces.

Interestingly, **Y002** is a material that exhibits the property of sublimation, indicating the transition from the smectic A phase to a gas phase (typically, sublimation refers to the transition from a solid to a gas phase). This sublimation can be attributed to the presence of a perfluoroalkyl chain within the molecule (Fig. 1b). The strong electronegativity of fluorine in perfluoroalkyl chains causes symmetric arrangement of dipoles, hindering intermolecular interactions due to a strong electrical barrier and a lack of induced dipole formation, leading to minimal dispersion force influence.(15, 34, 45) This property is effective even in the crystalline state, where the molecules are tightly packed. Due to the low intermolecular forces, the molecules in the outermost layer tend to escape from the surface with thermal stimuli, leading to sublimation. When TFCDs made of Y002 are thermally annealed at 160 °C on a flat silicone substrate or circular micro-post, an intriguing concentric semi-toroidal pattern is revealed within an hour (Fig. 1c, Fig. S3). Once the concentric hemi-cylindrical patterns form, they remain stable more than 90 minutes during the subsequent annealing process. The concentric hemi-cylindrical patterns appear to be associated with the internal organization of the TFCD assembly and exhibit a longer-lasting stability compared to the dimple structures. To analyze the distinctive structures formed from the sublimation process, it is essential to perform energy analysis of the changes occurring at the surface. The surface curvature of the TFCD consisting of Y002 plays an important role in describing the sublimation or evaporation rates. For this, with micro-pillars substrate, a single TFCD is isolated from the TFCDs film to observe a detail of curvature-evolution in the TFCD. The sublimation processes of Y002 on the Si substrate with micro-pillars have been carefully studied in order to better understand the TFCDs and their stability. The sublimation of the TFCD array on the Si substrate with micro-pillars was carried out by precisely controlling the depth of pillars in range of from 2 to 3 µm (Fig. 2a). Initially, similar to previous literature,(28) the cores of TFCDs are all placed onto the centers of circular pillars and satellite TFCDs are positioned between neighboring groups of four pillars (Fig. 2d). Subsequently, through a thermal annealing at 160 ℃ for ~ 1 hour, concentric hemicylindrical patterns of Y002 were formed on the pillars (Fig. 2b). These patterns are similar to those formed on a flat Si substrate, but they are all isolated within the pillars. Despite the significant sublimation occurring around the pillar vicinity at depths exceeding 5 µm, it is noteworthy that the concentric patterns on top of the pillar largely remain intact. This result is similar to the previously observed retention of concentric patterns on the top of the square micro pillars pattern from TFCDs film over the substrate.(34) The thermal stability of the evolved layering structures implies a lesser degree of sublimation from the concentric residue. This intriguing outcome emphasizes the complex interplay between the sublimation dynamics and the inherent structural characteristics of the TFCDs. To gain a clearer understanding of the sublimation process, the evolved topographies of the smectic layering were investigated through SEM images (Fig. 3). Initially, the sublimation occurs gradually, commencing from the highest layers on the film. Annealing takes place within a straightforward TFCD setup connected to its surroundings (as depicted in Fig. 2a, ii). Following its detachment from the surroundings (as shown in Fig. 2c), it assumes the form of a spindle torus. Subsequently, the droplet assumes a circular shape that persists until it reaches the core. Finally, the process results in the formation and isolation of a circular residue onto the pillar, which occupies precisely half the diameter of its TFCD (Fig. 2b, c). As the sublimation process progresses, it passes through a horn torus and becomes a ring torus (donut) shape. The bottom of the torus with the core layers corresponds to the central axis of the torus and remains the longest.

When a simple solid crystal sublimates from the surface, the molecular orientations and arrangements remain fixed and are exposed. Factors such as the local stress and strain relationship cannot be applied. In contrast, when evaporation occurs on the surface of an isotropic liquid, the molecular orientations dynamically change due to the free-flowing nature of the fluid, resulting in the continuous relaxation of partial stresses in droplets.(47-50) As a result, the structural characteristics of the interface are spontaneously and continuously relieved. LCs possess both crystalline order and fluidic behavior. Therefore, physical properties such as surface tension and viscosity, which are characteristic of liquids, still apply. Ultimately, Y002 is a crystalline fluid in the smectic phase, where structural loss occurs from the surface down to the layer level. It clearly exhibits distinct characteristics from the sublimation of simple solid crystals or the evaporation of isotropic liquids. The real-time morphological changes due to the surface tension during the sublimation process can be explained by the Bond number (Bo) of the fluid,(51)

where is the density, is gravitational acceleration 9.8 m/s², is the characteristic length, like the radius of curvature for a droplet, and is the surface tension. The Bond number is a dimensionless number that represents the importance of surface tension in a fluid system. When the Bond number is small (Bo << 1), surface tension dominates and has a pronounced effect on the surface morphology. On the other hand, when the Bond number is large (Bo >> 1), gravity becomes more significant, leading to different behaviors of the fluid. With a reference droplet size of 5.5 µm, Y002 demonstrates a Bond number in the range of 10⁻⁵, signifying that the influence of surface tension is sufficiently pronounced to remain largely unaltered by gravitational forces, thus directly manifesting in the surface morphology. However, it exhibits distinct characteristics compared to the evaporation of a simple isotropic liquid droplet.

Due to its high viscosity, Y002 experiences significantly limited flow within the system, resulting in restricted movement and deformation of the droplet. As a result, the stress induced by the droplet deformation remains prominent, and this is evident in the changes observed during the sublimation process. Meanwhile, since the outermost surface molecules are not firmly fixed, surface tension may affect the interface structure of droplets formed after sublimation. The Laplace number (La) is a dimensionless number that also represents the relative importance of viscous forces to surface tension forces in a fluid system. It provides a numerical measure of behavior differences between LC and isotropic liquids. It is defined as:

where is the viscosity. Reynolds number is a dimensionless number that represents the relative importance of inertia and viscosity in a fluid flow, and it determines the flow characteristics of the fluid. Weber number () is a dimensionless number that quantifies the relative importance of inertial forces to surface tension forces in a fluid system, providing insights into the behavior of fluid flows and the deformation of fluid interfaces. A large Laplace number signifies a significant ratio between surface tension and momentum transport within a fluid. The maintenance of fine droplet structures under conditions such as atomization is primarily described by the Laplace number.(52-54) It indicates that the influence of surface tension forces is relatively strong compared to the fluid's momentum, affecting the behavior and dynamics of fluid interfaces.

In contrast, the experiment using a non-circular elliptical pillar pattern yielded significantly different results.(Fig. 3) When the TFCDs were positioned on an ellipse with an eccentricity of 0.573 (Fig. 3b, left), their depth on the Y002 surface was comparatively shallower than in the case of a circular pattern. During the sublimation, irregular concentric residues resembling the TFCD structure were temporarily formed. These residues sublimated and disappeared relatively quickly. (Fig. S6) On the other hand, for an elliptical pillar with a larger eccentricity of 0.807 (Fig. 4b, right), achieving precise positioning of the TFCDs at the center proved considerably challenging. The resulting residue exhibited an irregular shape and tended to sublime rapidly, eventually vanishing completely. This finding suggests that the highly deformed smectic A layer structure becomes notably unstable. The observed instability is attributed to the asymmetric deformation that occurs when the smectic A layer forms TFCDs. In particular, it is expected that significant splay deformation occurs at the point corresponding to the long axis of the ellipse.

The thermodynamic properties of fluids are highly sensitive to the geometric structure of interfaces. In particular, the influence of interface curvature on phase transitions is described by the Kelvin’s or Young-Laplace equation.(51, 55, 56) It describes the relationship between the change in equilibrium vapor pressure and the curvature of an interface. The Laplace pressure, the difference of vapor pressure between the inside and the outside, denoted as , can be expressed as:

where is the surface tension. The unit normal vector, , is perpendicular to a surface at a given point toward outside. The term which represents the divergence of the unit normal vector, can be rewritten in terms of curvature. It is equal to twice the mean curvature (, which is the sum of the reciprocals of the principal radii of curvature

This equation relates the vapor pressure at a curved surface to the vapor pressure at a flat surface, the surface tension, the densities of the vapor and liquid phases, and the curvature of the surface. It provides a mathematical description of how the vapor pressure changes with the curvature of the surface. When the curvature is large (corresponding to smaller radii of curvature), the vapor pressure equation indicates an enhancement in the process of sublimation or vaporization. This means that in regions with significant curvature, where the surface is highly curved or sharply curved, there is a stronger tendency for molecules to undergo a transition to the vapor phase. In the case of an elliptical droplet, the Kelvin equation shows that there will be differences in vapor pressure occur between the sharp edges and the wider parts. This imbalance leads to asymmetric phase transitions, disrupting the stable TFCD structure formed by the smectic A phase. As a result, the system becomes more unstable and transitions into a less stable configuration. This phenomenon can be attributed to splay deformation, which causes increased thermodynamic activity due to molecular instability. The splay deformation of molecules in the curved regions results in an increase in the intermolecular spacing, reducing the cohesive forces between the molecules. As a result, the molecules in the curved regions have higher thermal energy, leading to an increase in the vapor pressure of the droplet.

Although the Kelvin equation provides a quantitative relationship between vapor pressure and droplet curvature, it assumes isotropic liquid and does not consider the effects of molecular order in the droplet. For example, while it is commonly used to describe the evaporation behavior of isotropic droplets, this equation is inadequate for explaining the complete evaporation dynamics of non-isotropic droplets, including those with a crystalline structure. This equation, based on the assumption of spherical symmetry, fail to account for the intricate internal organization and surface properties exhibited by non-isotropic droplets, making them unsuitable for accurate characterization of their sublimation behavior. The surface energy of the droplet is strongly influenced by the molecular ordering, and this needs to be considered when modeling the evaporation of non-isotropic droplets. An important next step based on the previous discussion is to understand how the deformation energy of smectic phases can be estimated and used to accurately model their behavior.

**Energy calculation and simulation**

The residue patterns that emerge following the sublimation of TFCD droplets result from the sublimation of the smectic A liquid crystal (LC) phase. This non-uniform sublimation process preferentially directs the evaporation or sublimation along specific orientations, giving rise to distinct residue patterns on the surface. The sublimation rate significantly influences the formation of these residue patterns. The speed at which TFCD droplets undergo sublimation determines the time available for the remaining material to reorganize, and during this period, surface tension aids in facilitating this reorganization. Therefore, the ultimate residue patterns observed after TFCD droplet sublimation are determined by the interplay between the surface tension of the smectic A phase and the sublimation rate. These patterns offer valuable insights into the surface properties and dynamics of the LC system, contributing to a deeper understanding of the behavior of this complex material.

Fig. 4 depicts the simulation results of the sublimation process of TFCD droplets, limited to circular or elliptical patterns, which are based on a phase-field model for a smectic interfacing an isotropic phase of different density.(57-59) The differentiation of smectic layer stacks is represented by the red and blue laminae (sinusoidal order parameter ), and the isotropic phase is shown in green (). The top-view images display the layers on the substrate surface where the torus droplets are located, with thick blue lines indicating the center circle of the tori, and the side-views reveal a center cross-section of the tori. The first case presents an initial order parameter configuration of a half spindle torus, with a focal conic at its center, using a grid of . The focal conic radius is , and the starting number of layers is 32. By simulating a heating treatment at a control parameter value higher than the coexistence one, , the smectic is destabilized and gradually sublimates into a small ring torus like configuration. The asymmetry in the interface evolution between the outer and inner part of the torus occurs because of the difference in mean curvature, particularly due to its change in sign close to the focal conic core.

The second set of simulation results in Fig. 4 mixes stretching and compression of layers with respect to the previous initial condition: the focal conic initial x-direction is stretched by 6.2/5.5 (), and the y-direction compressed by 5.2/5.5 (). For , besides the interface evolution taking place on top of the torus, we observe that layers close to the bottom slowly become unstable and disappear, so that a residual ring torus is not formed. The instability magnifies in the third case, where we stretch the initial layers by 7/5.5 in the x-direction () and compress by 3.4/5.5 in the y-direction ().

The elastic deformation energy of a smectic LC is a crucial factor in understanding its behavior and predicting its properties, which connects experimental observations to simulation results. For a nematic LC, the deformation energy that arises from distortions of the director field is described by the well-known Oseen-Frank elastic free energy. This energy functional presents contributions from the splay, twist, and bend deformation modes, which describe the energy cost of deforming the director field in different ways.

The Oseen-Frank free energy is given by the expression:

The distortion term of Oseen-Frank free energy is given by the expression:

where is the director field and , , and are the splay, twist, and bend elastic constants, respectively. For a smectic A, the twist and bend deformation modes of **n** are restricted, so that only the splay of molecules are allowed, which corresponds to bending of the smectic layers. Besides bending of layers, deviations from the equilibrium interlayer spacing also contribute to the smectic elastic energy, but we will not include them in this analysis. Since sublimation occurs at the outermost layers, there is no need to consider the interaction with the substrate. Therefore, the deformation energy density of the outermost layer of TFCD, considering the sublimation of torus-shaped droplets, can be abbreviated as follows:

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here, is the same term that appears in the Laplace pressure, which is twice the mean curvature of the TFCD outermost layer. This energy penalization is also present in the phase-field model we adopt, where the elastic constant can be related to the model parameters (see Supplementary Information).

In the case of an elliptical droplet, the asymmetric and pronounced sublimation at the pointed regions lead to an imbalance and structural deformation. Isotropic liquids, such as water or alcohol, which have relatively high fluidity, can easily alleviate this imbalance through the free flow of the fluid. However, in the case of smectic A phase and other viscous and anisotropic materials, this structural stress cannot be resolved and causes a discontinuous phase transition, making it very difficult to predict intermediate processes. Partial imbalances in the smectic A phase and other viscous and anisotropic materials can lead to the collapse of the structure, resulting in the formation of irregular and amorphous residues. (Fig. 3b and Fig. S5) This behavior highlights the intricate nature of the sublimation process in these materials, where the interplay between structural stress, phase transitions, and surface morphology becomes highly complex. These findings pave the way for advancements in the field of smectic liquid crystals and provide valuable insights for the development of novel applications and technologies.

**Smectic residual 3D lithography**

**Lastly, we investigated the thermally sublimed patterns that occur when a TFCD array is formed over a microchannel, based on the mechanism forming the hemicylindrical circular residuals that survives relatively longer. When TFCDs are formed within confined channels, their size and arrangement can be varied according to the depth and width of the channels. For example, when the Y002 is filled in microchannels of width 5 and depth 5 μm, the arrays of TFCDs show a linear pattern (Fig. S8), in which each array is independent of the other. However, when the TFCD film is formed thicker than the height of the channel, the arrangement of TFCDs, formed through planar anchoring-based epitaxial self-assembly of SmA LC molecules along the channel's terrain, can exhibit its typical hexagonal array by connecting the smectic layers in TFCDs (Fig. 5a). In the microchannel, the centers of TFCDs are positioned along its main direction and arranged in a staggered manner with respect to adjacent channels, resulting in the formation of a hexagonal array over the channels. Interestingly, as shown in SEM images (Fig. 5b) and the corresponding schematic sketches (Fig. 5c), the annealed structures of the TFCDs in the channel are considerably different from that of TFCDs on a flat substrate (Fig. 1c and Fig. S3), in which the hemicylindrical patterns is seemingly elongated perpendicular to the channel while the concentric patterns of the hemicylinders are revealed on the flat substrate. Concentrating on a single TFCD in the channel, initially it shows concentric patterns of the hemicylinders, which is highly similar to the patterns on flat substrate. With further annealing, the hemicylinders are seemingly transformed into elongated patterns across the width of channel (Fig. 5d).**

**Simulation results clearly represent the corresponding topographical evolution of annealed TFCDs confined in the channel, as observed from the hemicylinders’ modulation evolution on the bottom of the channel (Fig. 5e). These simulations use a grid of** , and an initial order parameter configuration consisting of a TFCD similar to the ones in experiments (Fig. 5d), whose film depth is higher than the channel’s height. Both the channel walls and the substrate present a neighborhood favoring the smectic and planar anchoring, to connect with the surface treatment of the substrate in experiments. As in the previous section, we use in the numerical experiments to simulate the annealing, so that the outer smectic layers sublime while the bottom layers restructure.

**The formation of a hemispherical cylinder structure in experiments is due to the partial rearrangement of Y002 molecules normal to the air interface, during the sublimation process of Y002 on the surface of TFCDs.(43) Therefore, it can be understood that the molecular alignment within the internal layers is always perpendicular to the long axis of the hemispherical cylinder. Based on this fact, by examining the intermediate structures that arise through the sublimation process in the layer-by-layer evaporation, the layered structure and molecular alignment within the initial TFCDs can be sequentially confirmed throughout its thickness. Thus, as observed with TFCDs' thermal annealing process on flat substrates and as inferred from the Maltese cross pattern of TFCDs observed through POM, it can be inferred that on flat substrates, molecular alignment at the bottom surface occurs radially with a defect-centered orientation. However, in the case of TFCDs on channel substrates, while POM images might not clearly distinguish them from those on flat substrates, SEM images of structures processed at 160 ℃ for 40 minutes reveal that the molecular alignment at the bottom of the channel is parallel to the long axis of channels (4th image in Fig. 5d), distinct from the radial orientation (Fig. S4). The above results introduce a new method for analyzing the internal structure of smectic LCs, which can complement the limitations of observation on layered LC structures using POM. Furthermore, it holds potential as a novel fabrication technique capable of hierarchically forming micro-nanostructures on the surface of three-dimensional structures.**

**Discussion**

In conclusion, our study has demonstrated the precise spatial control achieved by depositing smectic LCs on patterned silicon substrates and isolating TFCD in a well-defined arrangement. Sublimation of the LCs was used to indirectly assess the energy properties of the TFCD structures, with the thickness of the LC layer and parameters of the substrate pattern enabling the production of isolated TFCDs. These findings provide us with a greater understanding of the behavior of torus-shape droplets, and how their arrangement is greatly influenced by the shape of the patterned substrate. Simulation results reveal that the arrangement of TFCDs is greatly impacted by the shape of the patterned silicon substrate, and a geometric model was proposed to accurately estimate the energetic effects of nonzero eccentricity and evaluate their thermodynamic stability. This model can help us better understand the stability of the TFCD structures, and the parameters of the silicon substrate can be manipulated to produce unique patterns. Sublimation can be considered as a measure of molecular arrangement stability, with the more unstable the state, the faster sublimation occurs. In the elliptical shape, TFCD has a more distorted and unstable structure, thus leading to faster sublimation. Our findings provide valuable insights into the behavior of smectic LCs, and open up new possibilities for the development of novel LC-based devices with precise control over their topological properties. By manipulating the parameters of the silicon substrate, it is possible to create TFCD arrangements that are thermodynamically stable, and therefore less likely to be affected by sublimation. This can enable the production of unique patterns that can be used to develop novel LC-based devices.

**Materials and Methods**

**Materials**

All solvents were procured from commercial suppliers at reagent grade or higher purity. If required, they were further purified to eliminate any residual moisture or oxygen. 3-Butenoic acid (97%), heptadecafluoro-n-octyl iodide (98%), tetrakis(triphenylphosphine)palladium (99%), lithium aluminium hydride (95%), ethyl 3-(4-hydroxyphenyl) benzoate (98%) were purchased from Sigma-Aldrich. Potassium carbonate (99%) was purchased from Alfa Aesar. Carbon tetrabromide (99%), triphenylphosphine(95%) were purchased from TCI Chemicals.

**Synthesis of Ethyl 4’-[(5,5,6,6,7,7,8,8,9,9,10,10,11,11,12,12,12-heptadecaflourododecyl)oxy] [1,1’-biphenyl]-4-carboxylate (Y002)**

5,5,6,6,7,7,8,8,9,9,10,10,11,11,12,12,12-heptadecafluoro-1-bromododecane reacted with ethyl 3-(4-hydroxyphenyl) benzoate, leading to the final synthesis of Ethyl 4′-[(5,5,6,6,7,7,8,8,9,9,10,10,11,11,12,12,12-heptadecafluorododecyl)oxy][1,1′-biphenyl]-4-carboxylate (Y002). The synthesized compound underwent purification through multiple extractions using water and dichloromethane, with detailed information available in the Supplementary Information (SI).

**Sublimation procedure**

The following detailed process was carried out to effectively interact with the Si substrate by adjusting the depth of the sample. The Si substrate was pretreated with 100 W UV irradiation to generate oxygen plasma, which resulted in a hydrophilic surface on the substrate. In the first step of the process, Y002 material is deposited on a Si substrate that has been heated to approximately 200 °C, which leads to an isotropic state. Upon cooling to around 190°C, TFCD forms randomly on the surface. The temperature is then maintained to allow for slow sublimation to adjust the thickness. When the TFCD on the surface is observed under an optical microscope to begin being influenced by the pattern of the Si substrate, the substrate is reheated to 200°C in order to achieve an isotropic state (Figure 3a, i). It is rapidly cooled at a rate of 5°C/min and reaches a temperature of approximately 190-195°C. The sample undergoes a transition to the smectic A phase, and the formation of a uniformly distributed TFCD begins. Under the given conditions, arranging TFCD hexagonally is unfavorable, and it is strongly influenced by the pattern of the underlying Si substrate. Afterward, the sample is rapidly cooled to 160°C (at a rate of 50°C/min) and annealed for approximately 40 minutes.

**Observation**

Scanning electron microscope (SEM) samples were prepared through the application of an osmium plasma coater to deposit a conductive osmium layer. Imaging procedures were carried out utilizing a Hitachi SU-8230.

**Phase Field Model and Computational Methodology**

This work introduces simulations based on a weakly compressible model for smectic-isotropic interfaces, building upon previous phase-field models. The model describes a smectic phase in contact with an isotropic fluid of different density. Numerical integration of the governing equations captures complex transitions, and offers insights into how the alignment of layers and hemicylinders affect the interface thermodynamics and curvature driven evolution, demonstrating relevance to experimental observations. The smectic is represented by a sinusoidal order parameter linked to molecular density variations. The energy of the system accounts for displacement from planar layer configurations, and also for deviations from equilibrium interlayer spacing and densities. The energy density is expressed in terms of the order parameter and its derivatives, with a control parameter that can set which phase is energetically favored or allow both to coexist.

The governing equations encompass mass and momentum balances, as well as the smectic order parameter equation. These equations are numerically integrated using a pseudo-spectral method, with specific boundary conditions reflecting planar anchoring. The simulations capture transitions from initial TFCD configurations to conical pyramids and concentric rings, mirroring experimental observations. The surface tension and splay modulus can be written in terms of model parameters, and are tied to each other through those.

The simulations consider parameter settings in line with experimental data, ensuring a sensible ratio between splay modulus and surface tension. The chosen density penalization parameter remains small to account for heating effects and allow for sublimation to occur. Viscosity constants and mobility are specified, along with equilibrium densities for both phases. Further details are provided in the supporting information.

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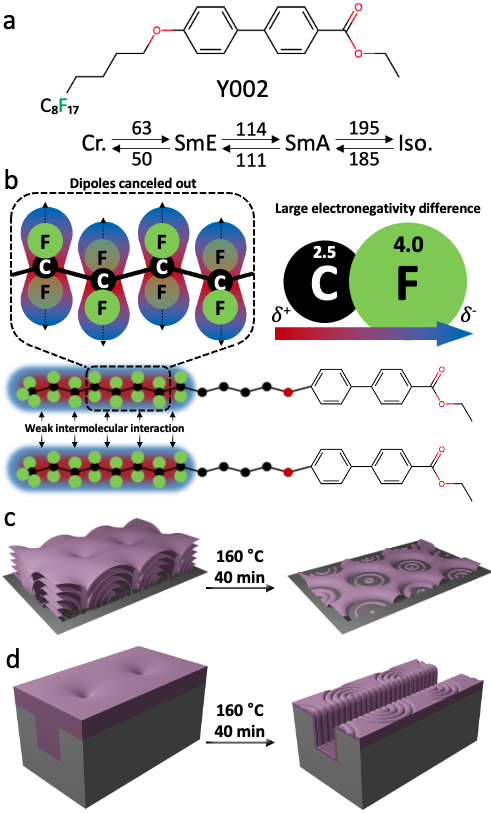
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[One column] Figure 1. a) Molecular structure and phase transition temperature of Y002. b) Appearance of strong dipoles formed by the large electronegativity of fluorine. These cancel out and less intermolecular induced polarization occurs. c) Schematic images of the TFCD structure composed of Y002 of the SmA phase on flat Si substrate and the concentric circle pattern formed after sublimation.

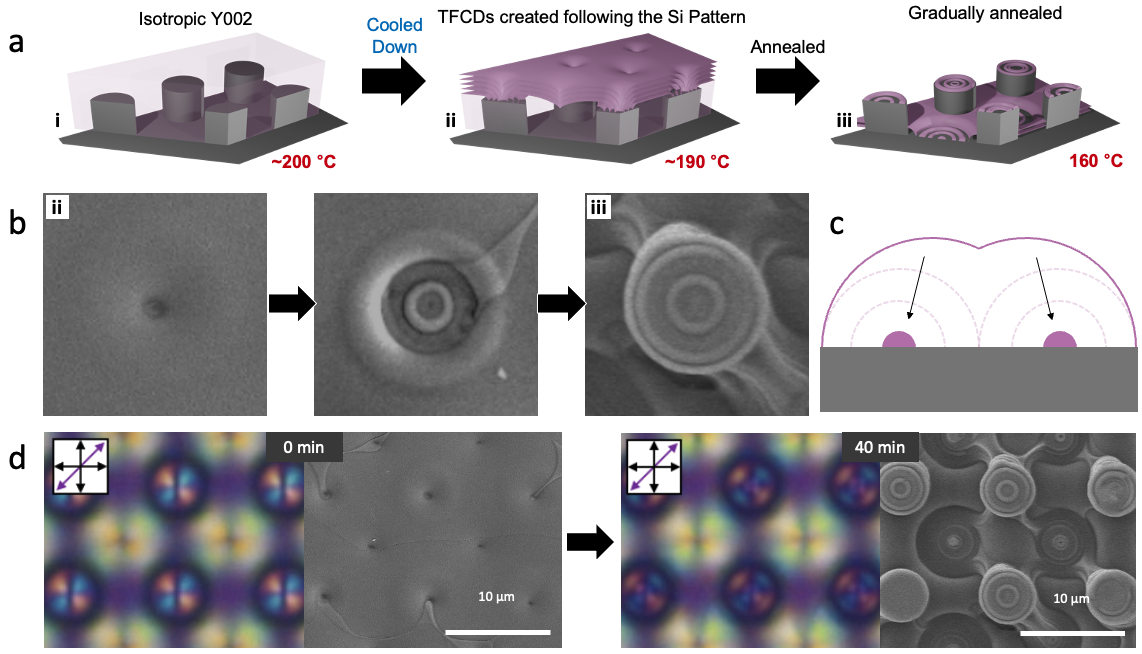


Figure 2. a) The sublimation process of Y002 on a Si pattern; i. The substrate is heated to 200 °C to achieve isotropic state. ii. When cooled at a rate of 5 °C/min, the arrangement of TFCDs is significantly influenced by the Si substrate pattern beneath the Y002 surface. iii. The TFCDs are annealed and fixed for less than an hour at 160°C. b) Top-view SEM images of sublimation process of Y002 in circular pillar patterns. c) Side-view schematic image of sublimation process of Y002 in circular pillar patterns. d) Sublimation process and schematic illustration of Y002 in circular pillar patterns array.

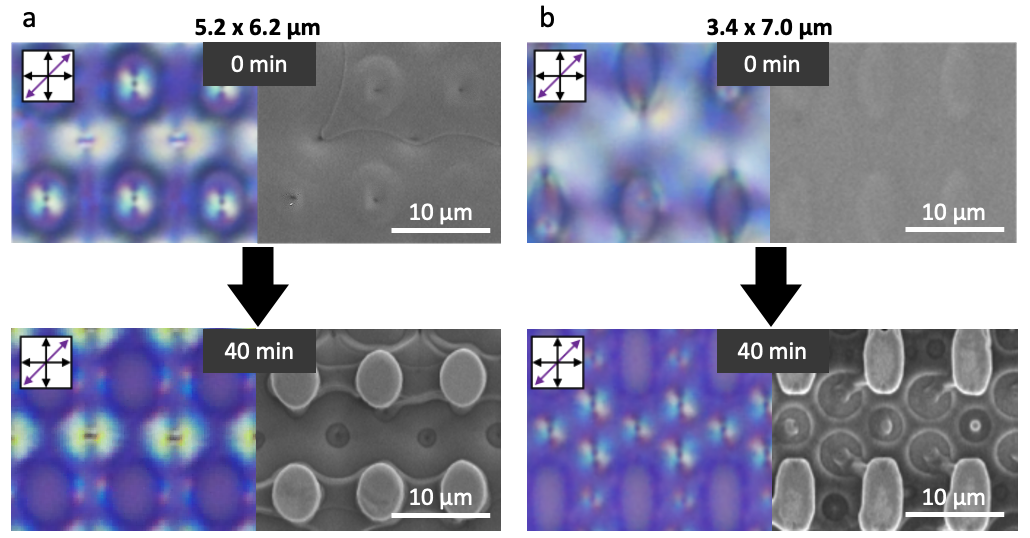


Figure 3. Sublimation process of Y002 in two elliptical pillar patterns. a) 5.2 x 6.2 µm, and b) 3.4 x 7.0 µm.

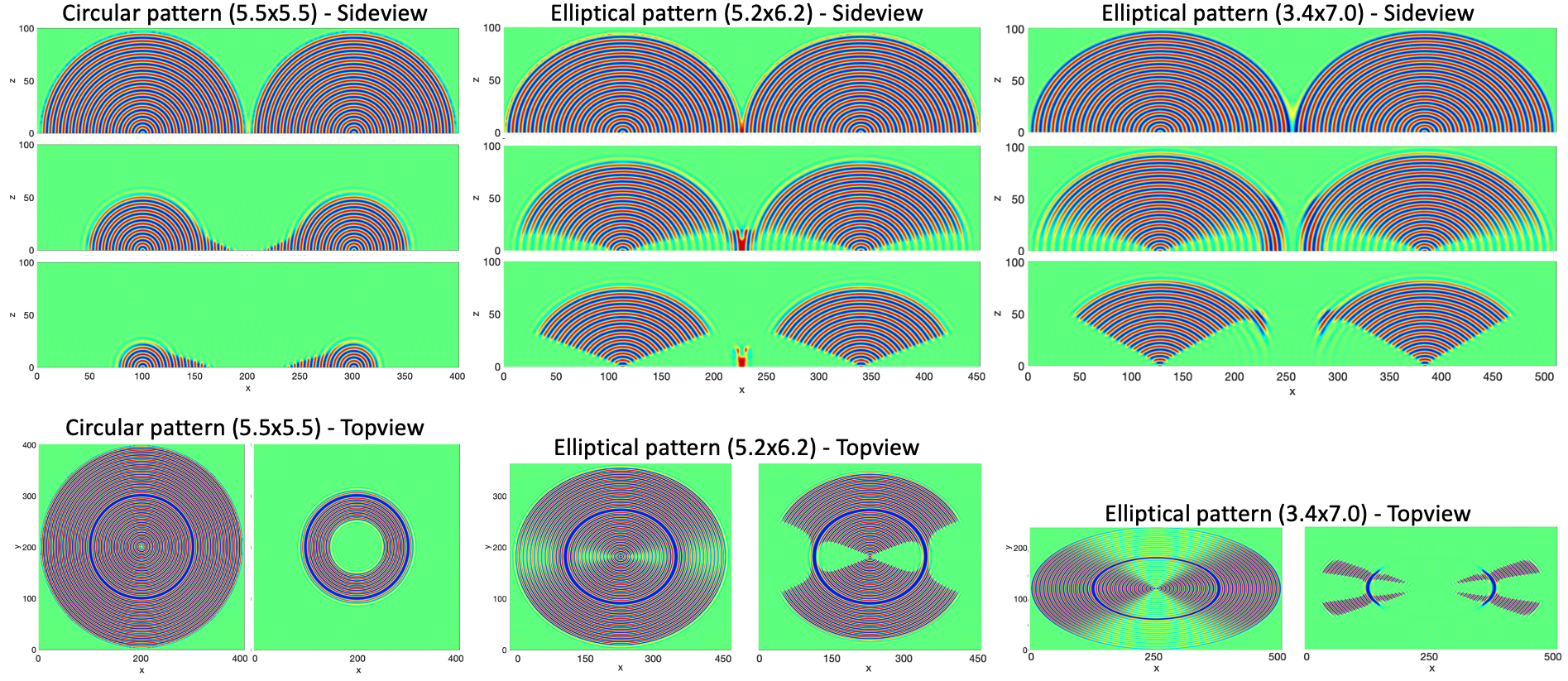


Figure 4. Simulation images of the TFCD droplet sublimation process, with an initial order parameter condition consisting of a half spindle torus with circular and elliptical bases. The blue and red lamellae represent the smectic layering, and the green is a distinct isotropic phase. The thick blue lines on topviews indicate the central circle of the torus.

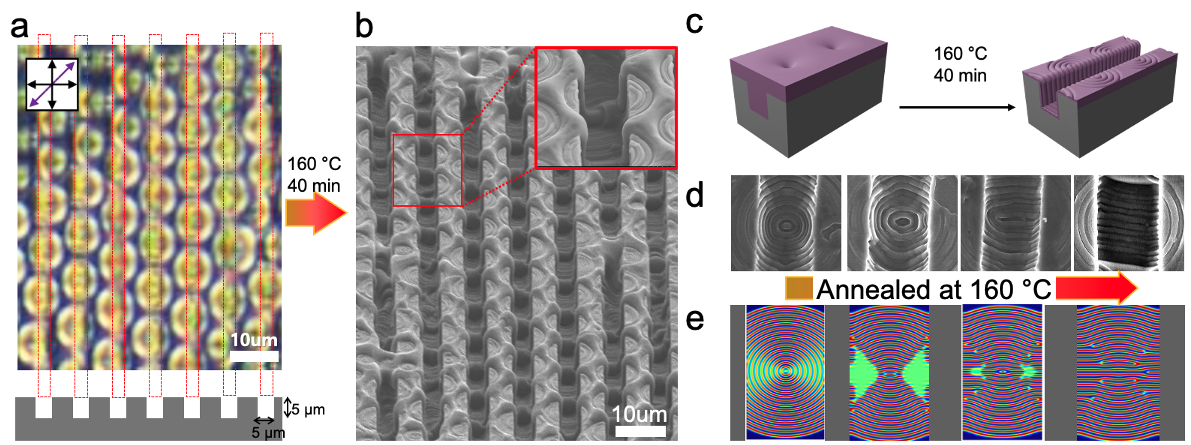


Figure 5. a) Polarized optical microscope (POM) and b) SEM images of sublimation process of TFCDs array on a 5 µm-channel patterned Si wafer. c) Schematic images of sublimation process of TFCDs array. d) Top view of SEM images of sublimation process of TFCDs array. e) Simulation comparisons corresponding to SEM images of each sublimation process.