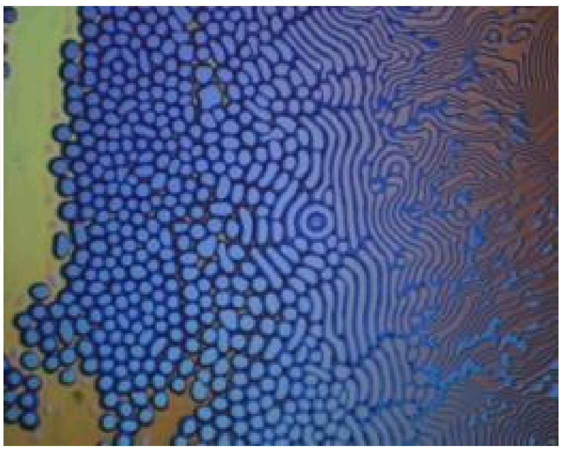
Experiments settle long-standing debate about mysterious array formations in nanofilms

May 19 2011, by Kathy Svitil



Transition between 3-D nanopillar arrays and striped structures in a polystyrene nanofilm subject to a thermal gradient of 100,000 degrees Celsius/cm. [Credit: Courtesy of E. McLeod and S. M. Troian, {LIS2T} lab/Caltech]

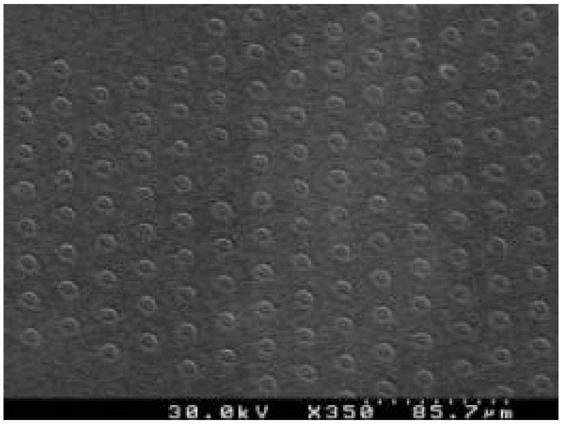
(PhysOrg.com) -- Scientists at the California Institute of Technology have conducted experiments confirming which of three possible mechanisms is responsible for the spontaneous formation of three-dimensional (3-D) pillar arrays in nanofilms (polymer films that are billionths of a meter thick). These protrusions appear suddenly when the surface of a molten nanofilm is exposed to an extreme temperature gradient and self-organize into hexagonal, lamellar, square, or spiral patterns.

This unconventional means of patterning films is being developed by Sandra Troian, professor of applied physics, aeronautics, and mechanical engineering at Caltech, who uses modulation of surface forces to shape and mold liquefiable nanofilms into 3-D forms. "My ultimate goal is to develop a suite of 3-D lithographic techniques based on remote, digital modulation of thermal, electrical, and magnetic surface forces," Troian says. Confirmation of the correct mechanism has allowed her to deduce the maximum resolution or minimum feature size ultimately possible with these patterning techniques.

In Troian's method, arbitrary shapes are first sculpted from a molten film by surface forces and then instantly solidified in situ by cooling the sample. "These techniques are ideally suited for fabrication of optical or photonic components that exhibit ultrasmooth interfaces," she explains. The process also introduces some interesting new physics that only become evident at the nanoscale. "Even in the land of Lilliputians, these forces are puny at best—but at the nanoscale or smaller still, they rule the world," she says.

The experiments leading to this discovery were highlighted on the cover of the April 29 issue of the journal *Physical Review Letters*.

The experiments, designed to isolate the physics behind the process, are challenging at best. The setup requires two smooth, flat substrates, which are separated only by a few hundred nanometers, to remain perfectly parallel over distances of a centimeter or more.



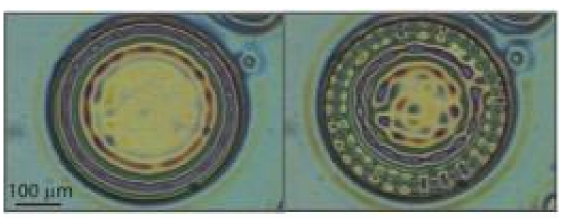
Scanning electron micrograph of solidified protrusions in a 98 nm polystyrene film guided by a remote hexagonal array of cold pins. [Credit: Courtesy of E. McLeod and S. M. Troian, {LIS2T} lab/Caltech.]

Such an experimental setup presents several difficulties, including that "no substrate this size is truly flat," Troian says, "and even the world's smallest thermocouple is too large to fit inside the gap." In addition, she says, "the thermal gradient in the gap can exceed values of a million degrees per centimeter, so the setup undergoes significant expansion, distortion, and contraction during a typical run."

In fact, all previous studies confronted similar challenges—leading to inaccurate estimates of the thermal gradient and the inability to view the formation and growth of the structures, among other problems. "To complicate matters," Troian says, "all of the previous data in the literature were obtained at very late stages of growth, far beyond the regime of validity of the theoretical models," Troian says.

The Caltech experiments solved these challenges by reverting to in situ measurements. The researchers replaced the top cold substrate with a transparent window fashioned from a single crystal sapphire, which permitted them to view directly the developing formations. They also used white light interferometry to help maintain parallelism during each run and to record the emerging shape and growth rate of emerging structures. Finite element simulations were also used to obtain much more accurate estimates of the thermal gradient in the tiny gap.

"When all is said and done, our results indicate that this formation process is not driven by electrostatic attraction between the film surface and the nearby substrate—similar to what happens when you run a comb through your hair—or pressure fluctuations inside the film from reflections of acoustic phonons—the collective excitations of molecules—as once believed, Troian explains. "The data simply don't fit these models, no matter how hard you try," she says. The data also did not seem to fit a third model based on film structuring by thermocapillary flow—the flow from warmer to cooler regions that accompanies surface temperature variations.



(Left) Emergent 3-D protrusions beneath a cold transparent cylindrical mesa (400 µm diameter) in a 160 nm polystyrene film subject to a thermal gradient of 240,000 degrees Celsius/cm. (Right) Formations after some have contacted the cold mesa. [Credit: Courtesy of E. McLeod and S. M. Troian, {LIS2T} lab/Caltech]

Troian proposed the thermocapillary model several years ago. Calculations for this "cold-seeking instability" suggest that nanofilms are always unstable in response to the formation of 3-D pillar arrays, regardless of the size of the thermal gradient. Tiny protrusions in the film experience a slightly cooler temperature than the surrounding liquid because of their proximity to a cold target. The surface tension of those tips is greater than that of the surrounding film. This imbalance generates a very strong surface force that "pulls" fluid up and "into the third dimension," she says. This process easily gives rise to large area arrays of dimples, ridges, pillars, and other shapes. A nonlinear version of the model suggests how cold pins can also be used to form more regular arrays.

Troian was initially disappointed that the measurements did not match the theoretical predictions. For example, the prediction for the spacing between protrusions was off by a factor of two or more. "It occurred to me that certain properties of the nanofilm to be input into the model might be quite different than those literature values obtained from macroscopic samples," she notes.

She enlisted the advice of mechanical engineer Ken Goodson at Stanford, an expert on thermal transport in nanofilms, who confirmed that he'd also noticed a significant enhancement in the heat-transfer capability of certain nanofilms. Further investigation revealed that other groups around the world have begun reporting similar enhancement in optical and other characteristics of nanofilms. "And voila! … by adjusting one key parameter," Troian says, "we obtained perfect agreement between experiment and theory. How cool is that!"

Not satisfied by these findings, Troian wants to launch a separate study to find the source of these enhanced properties in nanofilms. "Now that our horizon is clear, I guarantee we won't sit still until we can fabricate some unusual components whose shape and optical response can only be formed by such a process."

More information: The paper, "Experimental Verification of the

Formation Mechanism for Pillar Arrays in Nanofilms Subject to Large Thermal Gradients," was coauthored by Euan McLeod and Yu Liu of Caltech.

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