deposition. The researchers introduced defects in the BFO during the growth process by precisely controlling the temperature, gas pressure, pulse energy, pulse rate, and target composition. High-resolution images of the 60-nm-thick BFO film revealed a high-quality surface with uniformly distributed defects. The defects were larger than a single atom, with an average width of ~5 nm and height of ~2 nm. “Their structure is complex and has not been investigated in detail yet,” says Seidel.

To create a memory storage system, the team inserted a 3-nm-thick electrode between the BFO and substrate. Then, using the conducting tip of an atomic force microscope probe, they applied a voltage pulse across the film. The pulse created a stable nucleus of polarization in the film directly below the tip from which the domain spread outward. This spreading can be described by the motion of the domain walls. By systematically varying pulse duration and tip voltage while scanning the film, the team created domains of different sizes.

A statistical analysis of domain diameter as a function of voltage and duration revealed that activating the motion of a domain wall in the film required an electric field 3–6 times larger than in conventional BFO systems. This suggested that the defects exerted local strain that effectively pinned the domain walls in place.

To study the extent of the pinning, the researchers formed domains of various sizes using a tip voltage of –9 V and a pulse duration ranging from 5 ms to 200 ms. They imaged the film with high-resolution piezoresponse force microscopy, which simultaneously captured topography and ferroelectric domains, during a span of 8904 hours. Even after more than one year, the diameters of the domains remained essentially the same.

The normalized polarization retention of this system was at least one to two orders of magnitude better than other ferroelectric systems, the researchers reported. Furthermore, the stability persisted across domains of all sizes. This was surprising because small domains normally decay faster than large domains, and indicates the system’s potential for high-density memory applications that utilize small domains. With an optimally sharp tip, the researchers estimate they may be able to achieve a storage density up to 1300 Gbit/in^2.

“[This] work shows a promising path forward to producing superior high-density nonvolatile memories based on ferroelectric materials,” according to Matthew Dawber, an expert on ferroelectric materials at Stony Brook University, The State University of New York, who was not associated with this project. “[The researchers] show that introduced defects can help stabilize tiny domains for very long times. This is a win-win, normally it’s hard work to get rid of defects, and conversely, it’s not too hard to introduce them,” Dawber says.

The team focused on one kind of defect in this research, but Seidel says that there are many options for pinning domain walls and further improvement may be possible. “Another interesting aspect is the intrinsic properties of domain walls themselves, which can be exploited for nanoelectronics,” he says. “[Domain walls have] been known for a long time, but insight into their intrinsic properties and functionality has been investigated in more detail only recently.”

Kendra Redmond

Nano Focus

Parallelized two-photon lithography enables submicrometer additive microfabrication

Additive microfabrication—three-dimensional (3D) printing on the micron and submicron level—is relatively new and is expected to have a broad niche market especially in biomedical and wearable electronics industries. The available microprinting techniques, however, suffer from either low throughput that constrains their scaling up to mass production, or poor resolution on the micron scale. A team of researchers has increased the printing speed by more than 1000-fold without sacrificing resolution of the printed pattern. The research team at Lawrence Livermore National Laboratory (LLNL) and The Chinese University of Hong Kong, led by Sourabh K. Saha and Shih-Chi Chen, succeeded in parallelizing two-photon lithography (TPL), a higher resolution lithography method.

TPL is typically a serial method where submicron patterns are printed in a sequential manner rendering it too slow to be practical. The researchers developed a technique where TPL was used to print large areas simultaneously without sacrificing the resolution of the structures that reached length scales as small as 130 nm. The technique, as introduced in a recent issue of *Science* (doi:10.1126/science.aax8760), parallelized TPL-based microfabrication by combining technologies from laser physics, digital optics, and 3D printing.

In two-dimensional (2D) lithography, a 2D pattern is printed on a photosensitive polymer (resist) by exposing it to focused light or a laser through a patterned mask; areas exposed to the light are chemically altered (cured/polymerized) while those covered by the mask are not. By changing the solubility of the exposed volume, a 2D pattern emerges after submerging the polymer into a solvent. The idea was to achieve 3D printing by printing 2D layers on top of each other creating 3D structures.

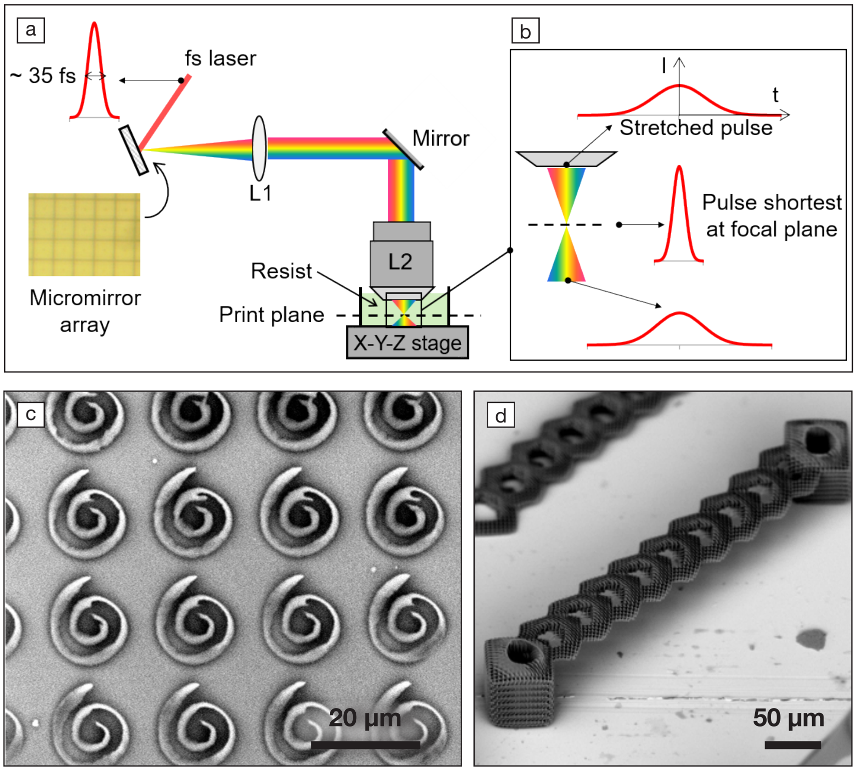
The main challenge that the researchers overcame was patterning a thin sheet of the polymer while leaving the lower and upper layers unaffected. This allowed layer-by-layer printing by moving a new sheet of the uncured polymer into the focal plane of the laser. The new technique accomplished just that by simultaneously focusing a pulsed near-infrared laser in the time and space domains and thus creating a thin, temporally focused light sheet.

“This was implemented by focusing patterned laser pulses in the time domain such that it has the shortest duration and highest intensity at the spatial focal plane. Basically, the laser pulse was stretched and then compressed in the desired plane, a technique used in designing high-power ultrafast lasers,” says Saha, now an assistant professor at the Georgia Institute of Technology.

"By stretching the pulse, its intensity becomes too weak to polymerize the resist, and by designing the optical system such that the pulse is shortened in the focal plane we managed to control the intensity of the laser and consequently the polymerization of resist in the axial (third) dimension," says Chen, an associate professor at The Chinese University of Hong Kong. The pulse stretching was achieved by exploiting the patterning mask, a collection of digital micromirrors, as a diffraction grating to disperse a broadband femtosecond laser into its constituent wavelengths and accordingly increasing the pulse duration. The setup could be used to print features as small as ~130 nm.

The researchers could print large areas of 165 μm × 165 μm in a matter of milliseconds. "In conventional TPL, a focused laser spot traces a pattern. So, printing a centimeter-sized object could take a year," Chen says. The attained speed did not affect the resolution; structures smaller than the optical diffraction limit were achieved by changing the beam power and exposure due to the nonlinear absorption mechanism.

"The parallel two-photon lithography system breaks the coupling between nanoscale feature size and slow build speeds," says Christopher Spadaccini, director of the Center for Engineered Materials, Manufacturing and Optimization at LLNL, who was not involved in the study. The technique enabled high resolution to be realized in the axial direction, as among the most challenging goals in additive microfabrication. Chen says, "We managed to confine the laser axially to a couple hundred nanometers, an improvement over conventional methods." Another important accomplishment of the technique is the capacity to print features difficult to achieve with any other method such as curved structures and suspended bridges.



(a) Schematic of the microfabrication setup. L1 refers to the collimating lens and L2 refers to the objective lens that focuses the pulse in the time domain. The mirror is a collection of digital micromirrors that are switched on or off to pattern the reflected laser. (b) Zoomed-in illustration of the temporal focusing where the shortest pulse is only achieved at the focal/print plane. (c) Spiral structures printed in single-digit millisecond time scales without any stage motion. (d) Bridge structure printed by multiple 2D projections. The structure is generally difficult to print using other techniques. Credit: *Science*.

This achievement opens the door to many applications spanning health care to energy and metamaterials. "The demonstrated 3D microprinting with submicron resolution and unprecedented rates opens numerous applications in microrobotics, drug delivery, tissue engineering, wearable electronics, and sensors industries," says Andrei Kolmakov, project leader at the National Institute of Standards and Technology (NIST), who conducts research on high-resolution 3D printing with focused electron and x-ray beams. He was not involved in this study.

"Through this new technique, there is now a path to high-throughput nanoscale printing making it practical for real-world applications beyond the study of nanoscience and engineering. We have the setup built by Dr. Saha in the lab and are excited to work with him to apply it in new areas," Spadaccini says. Chen shares the same enthusiasm for the next step: "We are now looking on how to scale it up to make functional structures and exploring different optical methods to manipulate the temporally focused light sheet."

The technique is a breakthrough for resolutions down to ~100 nm. Achieving resolution in the single-digit nanometer scale in additive manufacturing remains a challenge. However, groups at Oak Ridge National Laboratory and NIST have already managed to reach features as small as a few nanometers using electron beams. Scaling up printing at such high resolutions is still at the forefront of research in this field.

Nora M. Hassan