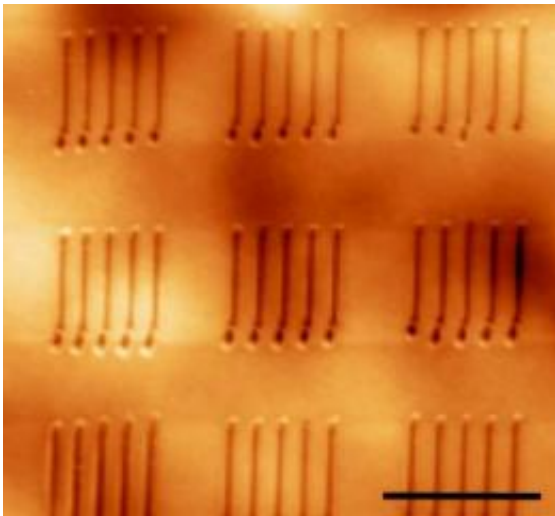


Heated AFM tip allows direct fabrication of ferroelectric nanostructures on plastic

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This image shows the topography (by atomic force microscope) of a ferroelectric PTO line array crystallized on a 360-nanometer thick precursor film on polyimide. The scale bar corresponds to one micron. Credit: Courtesy Suenne Kim

Using a technique known as thermochemical nanolithography (TCNL), researchers have developed a new way to fabricate nanometer-scale ferroelectric structures directly on flexible plastic substrates that would be unable to withstand the processing temperatures normally required to create such nanostructures.

The technique, which uses a heated [atomic force microscope](#) (AFM) tip

to produce patterns, could facilitate high-density, low-cost production of complex ferroelectric structures for energy harvesting arrays, sensors and actuators in nano-electromechanical systems (NEMS) and micro-electromechanical systems (MEMS). The research was reported July 15 in the journal [Advanced Materials](#).

"We can directly create [piezoelectric materials](#) of the shape we want, where we want them, on flexible substrates for use in energy harvesting and other applications," said Nazanin Bassiri-Gharb, co-author of the paper and an assistant professor in the School of Mechanical Engineering at the Georgia Institute of Technology. "This is the first time that structures like these have been directly grown with a CMOS-compatible process at such a small resolution. Not only have we been able to grow these ferroelectric structures at low substrate temperatures, but we have also been able to pattern them at very small scales."

The research was sponsored by the National Science Foundation and the U.S. Department of Energy. In addition to the Georgia Tech researchers, the work also involved scientists from the University of Illinois Urbana-Champaign and the University of Nebraska Lincoln.

The researchers have produced wires approximately 30 [nanometers](#) wide and spheres with diameters of approximately 10 nanometers using the patterning technique. Spheres with potential application as [ferroelectric memory](#) were fabricated at densities exceeding 200 gigabytes per square inch – currently the record for this perovskite-type ferroelectric material, said Suenne Kim, the paper's first author and a postdoctoral fellow in laboratory of Professor Elisa Riedo in Georgia Tech's School of Physics.

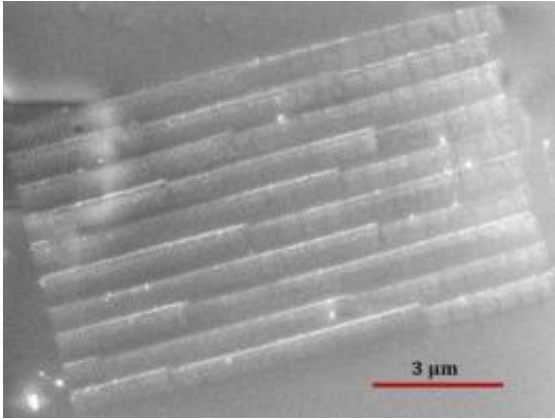
Ferroelectric materials are attractive because they exhibit charge-generating piezoelectric responses an order of magnitude larger than those of materials such as aluminum nitride or zinc oxide. The

polarization of the materials can be easily and rapidly changed, giving them potential application as random access memory elements.

But the materials can be difficult to fabricate, requiring temperatures greater than 600 degrees Celsius for crystallization. Chemical etching techniques produce grain sizes as large as the nanoscale features researchers would like to produce, while physical etching processes damage the structures and reduce their attractive properties. Until now, these challenges required that ferroelectric structures be grown on a single-crystal substrate compatible with high temperatures, then transferred to a flexible substrate for use in energy-harvesting.

The thermochemical nanolithography process, which was developed at Georgia Tech in 2007, addresses those challenges by using extremely localized heating to form structures only where the resistively-heated [AFM tip](#) contacts a precursor material. A computer controls the AFM writing, allowing the researchers to create patterns of crystallized material where desired. To create energy-harvesting structures, for example, lines corresponding to ferroelectric nanowires can be drawn along the direction in which strain would be applied.

"The heat from the AFM tip crystallizes the amorphous precursor to make the structure," Bassiri-Gharb explained. "The patterns are formed only where the crystallization occurs."



Scanning electron microscope image shows a large PZT line array crystallized on a 240-nanometer thick precursor film on a platinized silicon wafer. Credit: Courtesy of Yaser Bastani

To begin the fabrication, the sol-gel precursor material is first applied to a substrate with a standard spin-coating method, then briefly heated to approximately 250 degrees Celsius to drive off the organic solvents. The researchers have used polyimide, glass and silicon substrates, but in principle, any material able to withstand the 250-degree heating step could be used. Structures have been made from $\text{Pb}(\text{ZrTi})\text{O}_3$ – known as PZT, and PbTiO_3 – known as PTO.

"We still heat the precursor at the temperatures required to crystallize the structure, but the heating is so localized that it does not affect the substrate," explained Riedo, a co-author of the paper and an associate professor in the Georgia Tech School of Physics.

The heated AFM tips were provided by William King, a professor in the Department of Mechanical Science and Engineering at the University of Illinois at Urbana-Champaign.

As a next step, the researchers plan to use arrays of AFM tips to produce

larger patterned areas, and improve the heated AFM tips to operate for longer periods of time. The researchers also hope to understand the basic science behind ferroelectric materials, including properties at the nanoscale.

"We need to look at the growth thermodynamics of these ferroelectric materials," said Bassiri-Gharb. "We also need to see how the properties change when you move from the bulk to the micron scale and then to the nanometer scale. We need to understand what really happens to the extrinsic and intrinsic responses of the materials at these small scales."

Ultimately, arrays of AFM tips under computer control could produce complete devices, providing an alternative to current fabrication techniques.

"Thermochemical nanolithography is a very powerful nanofabrication technique that, through heating, is like a nanoscale pen that can create nanostructures useful in a variety of applications, including protein arrays, DNA arrays, and graphene-like nanowires," Riedo explained.

"We are really addressing the problem caused by the existing limitations of photolithography at these size scales. We can envision creating a full device based on the same fabrication technique without the requirements of costly clean rooms and vacuum-based equipment. We are moving toward a process in which multiple steps are done using the same tool to pattern at the small scale."

Provided by Georgia Institute of Technology

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