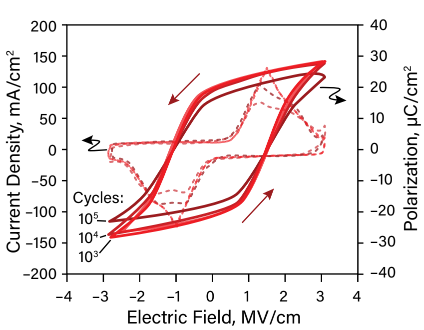
# Atomic Layer Deposition Techniques Promise Enhanced Piezoelectrics

Every year, the ceramic capacitor industry produces billions of capacitor units composed of piezoelectric, ferroelectric, and dielectric materials for applications including radio frequency (RF) communication, electric power coupling and stabilization, implantable medical devices, and automotive control. To address the expanding demand for smaller devices with less power consumption, manufacturers are seeking to augment historical tape casting, extrusion, and screen printing, which are typically limited to micron-scale features, with new sustainable chemical manufacturing methods that can form thinner materials in more complex geometries.

Researchers in the Industry-University Cooperative Research Center for Dielectrics and Piezoelectrics (CDP) at the Pennsylvania State Univ. and North Carolina State Univ., with support from the U.S. National Science Foundation (NSF), are collaborating with industry researchers to explore new materials and fabrication techniques for advanced dielectric and piezoelectric devices.




▲ **Figure 1.** Current density and polarization of a thin-film HZO ferroelectric formed by atomic layer deposition (ALD) are shown here. The dark lines show that when the voltage is increased, the bonds in the film become polarized. When the voltage decreases, the polarization remains present (unlike common dielectrics) until it is "switched off" again at lower voltages. By measuring polarization under no applied field, the material "remembers" the field that was most recently applied. The fainter lines show the current corresponding to the polarization switching. This switching can be repeated more than $10^5$ times.

Dielectrics are materials that become electrically polarized when exposed to an electric field, and piezoelectrics are a form of dielectric that become electrically polarized when mechanically stressed. As a special type of piezoelectric, ferroelectrics can maintain an electrically polarized state even after the polarizing force is removed, making them a possible option for storing large amounts of energy and small "bits" of computer information.

Since the early 2000s, hafnium dioxide ($HfO_2$) has been used as a critical gate dielectric in advanced semiconductor transistors. In the early 2010s, $HfO_2$ and mixtures of $HfO_2$ with $ZrO_2$ (*i.e.,* $Hf_xZr_{1-x}O_2$, or "HZO") were found to also have ferroelectric properties. Figure 1 shows polarization switching in a ferroelectric HZO thin film formed in a CDP lab by atomic layer deposition (ALD), a form of chemical fabrication.

Because the dielectric permittivity and piezoelectricity can change with film geometry, the ability to control the thickness of a dielectric or piezoelectric layer is very important. To understand the means to regulate piezoelectric materials with nanoscale precision, CDP PhD students Alex Hsain and Younghwan Lee, working with Jacob Jones and Greg Parsons at NC State, explored ALD to synthesize ferroelectric HZO. ALD is widely used for thin-film deposition in large-scale semiconductor manufacturing to create insulating coatings on complex non-planar surfaces with thicknesses controlled at the sub-nanometer level.

In one example study, the students used *in situ* high-temperature X-ray diffraction to understand the role of Hf:Zr ratio on crystallization behavior. The team further discovered that by forming the full metal/dielectric/metal material stack by ALD in a closed reactor system, the desired film stoichiometry could be controlled with thicknesses down to 10 nm, yielding good device performance and reduced oxygen impurities at the critical top and bottom metal/dielectric interfaces. By evaluating different oxygen sources, the students also discovered that they could manipulate the crystallographic texture near the bottom electrode. Understanding how surface chemistry influences crystal structure is important because forming crystalline thin films at low temperatures will open new opportunities to design, operate, and manufacture future electronic materials and systems that provide improved performance while also consuming less energy.

The positive results have spawned further CDP research to explore other ALD thin-film processes for piezoelectric materials. While this work advances fundamental understanding of ALD-based materials, the CDP's academic-industry partnership continues to identify opportunities for technology transfer and product innovation at member companies. Through CDP, industrial and academic researchers with complementary capabilities collaborate to address current problems, as well as build new knowhow for future challenges yet to be discovered.

Jerry Kolbe, Director of Corporate Technology and Innovation at CDP member company Murata Electronics, comments, "The ALD work that Greg and Jacob are doing in the CDP is state-of-the-art with a compelling potential for innovative process development that can deliver new value for industry." CEP

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