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Lifting the fog in ferroelectric thin-film synthesis



Frustrated by reproducibility in electrical measurements on ferroelectric films, Lane Martin, Jon-Paul Maria and Darrell Schlom discuss tactics to reliably synthesize ‘good’ ferroelectric samples, especially in the search for superior materials and device heterostructures.

“**T**he definition of insanity is doing the same thing over and over again and expecting different results.” This quote, often misattributed to Einstein¹, all too often describes the synthesis of ferroelectric thin films. What are the ways in which we can avoid repeating what are ostensibly the same growth conditions in hopes that the ($n + 1$)th attempt will yield a ‘good’ ferroelectric sample? The avalanche of emerging applications for ferroelectric films should draw us together as a community to carefully consider reproducibility in this field. Here, we address the challenges underlying accurate and reproducible growth of thin films, approaches that can be used for more reproducible determinations of ferroelectric properties, and trends regarding these methodologies.

The lure of ferroelectrics is increasing as we move into the second century of this intriguing and useful phenomenon. For applications including next-generation logic and memories, nano-electromechanical systems, components in microwave communications, and sensors and actuators, thin-film ferroelectrics are essential. Nonetheless, the field faces challenges. Whereas effects such as piezoelectricity and pyroelectricity are fundamentally related to material symmetry, ferroelectricity has an empirical definition—materials that exhibit two or more orientational states in the absence of an electric field and can be switched from one to another state using an electric field. To prove that a material is ferroelectric, it must electrically switch before it suffers electrical breakdown. Although the ferroelectric state was infrequently observed in the past, it has now become apparent that ferroelectrics are ubiquitous². We need improved methods of making and discerning potential ferroelectrics with clarity.

The properties of ferroelectrics are intimately linked to atomic structure, composition and the synthesis process. This is exacerbated by the fundamental order parameter of ferroelectrics (the polarization) being directly tied to the structure of the material such that structural distortions alter the polarization. Thus, anything that affects the structure can affect the ferroelectric properties. Today, a slew of methods are used to produce ferroelectric films, each with its own energetics, kinetics and regard for equilibrium thermodynamics. Even from a single laboratory, a film of the same material produced using different (or even the same) methods might yield completely different properties. For example, recent explorations of classic ferroelectrics—such as BaTiO₃ (ref. 3), PbTiO₃ (ref. 4) and BiFeO₃ (ref. 5)—reveal complex connections among intrinsic point defects and defect complexes with ferroelectric properties. This has led to defect-engineering routes to manipulate these materials⁶. Likewise, in the wurtzite-based ferroelectrics, things are even more complicated because ferroelectricity is observed in solid solutions at compositions that can be stable (Al_{0.94}B_{0.06}N) or highly metastable (Zn_{0.65}Mg_{0.35}O and Al_{0.7}Sc_{0.3}N). In either case ferroelectricity is present, but these materials lie close to a compositional instability or phase boundary. Furthermore, in the metastable formulations, it is nearly impossible to identify the exact crystal structure because different synthesis routes will produce differently quenched states. Taken together, there are some collective lessons for the community.

Make what you say and know what you make—the days of assuming that any growth technique can produce a complex multicomponent ferroelectric with little effort are gone. Researchers must increasingly understand that the ‘best’ properties for ferroelectrics

do not always come from stoichiometric materials.

Pay attention to the imaginary permittivity—it is critically important to quantify the loss. When materials become lossy (which can be hard to avoid in ferroelectrics at the high fields needed to switch), the polarization, permittivity and piezoelectricity become increasingly difficult to determine without ambiguity. When situations become challenging, resort to frequency, electric-field and temperature dependencies to fortify interpretive power.

Everything matters—in our experience, seemingly minuscule changes in synthesis conditions or parameters, substrate mounting, laser-beam conditioning, sputter-target poisoning, substrate cleaning or conditioning, and the pre-ablation, pre-evaporation and pre-sputtering times can each have substantial effects. The same holds for the formation of electrodes, where exposure to air, etching or annealing can also dramatically alter the electrical leakage and shift hysteresis curves. Well-documented synthesis data are critical to navigating the synthesis space and to re-finding a desired location. We need to improve instrumentation to facilitate this process.

Failures can be as important as successes—all too often we focus solely on what worked. Reporting common failure modes helps others to avoid getting stuck in the same local minima. Sharing complementary details builds understanding, even though it might seem foggy at first.

Stand on the shoulders of thermodynamics whenever possible—thermodynamics underlies the growth of compound semiconductors with reproducible properties. In the case of GaAs, defect contents of 1 atom in 10¹⁰ have been achieved, leading to record mobilities⁷. This is not because the gallium and arsenic were physically controlled to arrive at the surface with a 1:1 ratio; instead, the films were grown in a regime where thermodynamics

automatically led to the desorption of the excess arsenic supplied. Some ferroelectrics may be grown in an adsorption-controlled regime in which, analogous to the growth of GaAs, the film stoichiometry is controlled by thermodynamics. These include PbTiO_3 , $\text{Bi}_4\text{Ti}_3\text{O}_{12}$, BiFeO_3 and BaTiO_3 . Although this is a powerful method, remember that single-phase is not synonymous with stoichiometric. It depends on the phase diagram and, unfortunately, for many ferroelectric materials the phase diagrams are lacking. Moreover, arising from the empirical definition of ferroelectricity, there is a tendency for the field to occasionally “go bananas”⁸ and report spurious results that distract researchers into unfruitful pursuits. The influence this can have on the community can be profound, as was seen when many discounted the initial reports of ferroelectricity in HfO_2 -based materials⁹.



Multimodal approaches—we should embrace complementary approaches to establish the presence of ferroelectricity and only then apply the term. Ferroelectrics are non-centrosymmetric, piezoelectric, polar materials that can be switched. As such, multiple probes can be applied to separately assess non-centrosymmetry (such as second-harmonic generation), the presence of polar order (such as polar mapping based on scanning transmission electron microscopy and pyroelectric measurements), the presence of a transition temperature (such as temperature-dependent dielectric constant), switching experiments (preferably in a capacitor-based structure) and more. Reliance on any one technique lessens confidence in the conclusion.

Know the limitations—for example, while piezoresponse force microscopy has been an essential tool in the study of ferroelectric thin films, the observation of ‘poling’ alone using this approach should not be used to label a material as ferroelectric in the absence of other evidence. Contrast thought to arise from piezoresponse force microscopy could instead be due to electrostatic forces arising from the charge being deposited on the surface of the film by the conducting tip to which a bias has been applied. Finally, if the data support only that a material is polar, it should not be labelled ferroelectric without proof of switching.

Publish the details—as a community, we should bring back the experimental procedure! Methods sections are often found outside the main text of scientific papers and printed in smaller font, thus diminishing their importance. A detailed description of synthesis will improve our science and enhance collective progress. As authors, we should write more meaningful content and, as reviewers, we should require it.

Every day brings enticing ferroelectric candidates to study and impactful applications are growing rapidly. That said, we need to come to terms with what it takes to reproducibly produce these chemically diverse systems, to assess their stability and to rationalize their (sometimes) exotic behaviour. We may also ask whether these are truly novel phenomena or simply artefacts of the measurement process on new materials. We should continue to push the limits of materials in terms of size (thickness and lateral scaling), time (switching speed) and energy (pushing to the minimum voltage/energy for response).

To transition ferroelectrics from the materials of the future to the materials of today, we must not forget the basics and lessons from the past while remaining simultaneously open to new concepts, mechanisms and materials.

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Competing interests

The authors declare no competing interests.