PERSPECTIVES: MATERIALS SCIENCE

Orienting Ferroelectric Films

R. Ramesh and D. G. Schlom

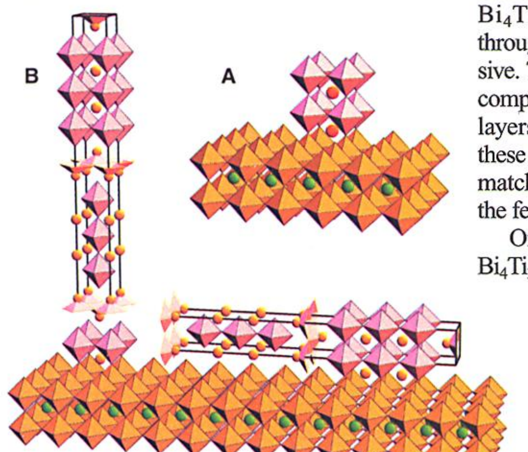
As silicon technology continues to dominate the microelectronics market, researchers around the world are looking at new ways to combine silicon with other materials in new devices. One of the key goals is the integration of functional materials, such as ferroelectric oxides, with silicon technology to produce commercially viable high-density, nonvolatile memories and other technologies (*1*).

First and foremost, this integration requires the ability to grow highly ordered thin ferroelectric films on silicon and other semiconductor surfaces. But crystallographic order is not enough: To maximize performance, the films also need to be oriented in particular ways, and the interface between film and substrate must be controlled. On page 2006 of this issue, Lee *et al.* (*2*) show how optimal control of crystallographic orientation can be achieved for a class of layered ferroelectrics that have been particularly challenging to grow.

Some ferroelectrics have the perovskite structure (see the upper figure, A); others have perovskite-related structures. The spontaneous polarization of layered perovskite-related ferroelectrics is generally quite small along the *c* axis but much larger along the *a* axis. Piezoelectric properties are similarly dependent on direction. This is why researchers are trying to control the crystallographic orientation of films of these materials.

Two important examples are the superconductor $YBa_2Cu_3O_{7-\delta}$ and the ferroelectric $Bi_4Ti_3O_{12}$. In the former, three cubic perovskite units are stacked to create a layered structure. In contrast, in $Bi_4Ti_3O_{12}$ pyramidal Bi_2O_2 layers alternate with structurally distinct tripled-perovskite layers (see the upper figure, B). This difference between the two materials is crucial when it comes to controlling their orientation.

In the case of ferroelectric perovskites, high-quality epitaxial films can be grown on silicon through the use of structural templates and chemical buffer layers between the silicon substrate and the ferroelectric film (*3–6*). The key to controlling their orientation is that the perovskite structure has comparatively little structural anisotropy (it

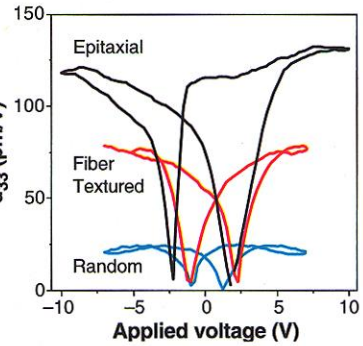


The key to alignment. Epitaxial alignment at growth temperature between a perovskite substrate and a thin film of **(A)** *c* axis–oriented $Pb(Zr,Ti)O_3$ (PZT), and **(B)** *c* axis–oriented (left) and (110)-oriented (right) $Bi_4Ti_3O_{12}$. The film orientations given are for the low-symmetry form of the materials after cooling to room temperature.

is essentially cubic at the growth temperature) and that the crystallographic orientation and crystalline perfection are therefore controlled by the "template" surface.

When the template surface is a cubic perovskite (or has a similar crystal chemistry in terms of oxygen coordination), epitaxial growth is facilitated. Conductive perovskite layers such as $(La,Sr)CoO_3$ or $SrRuO_3$ can be used to provide a bottom electrode that is also a suitable epitaxial template for growth of the overlying perovskite ferroelectric. The resulting optimally oriented epitaxial layer has improved piezoelectric properties (see the lower figure).

Can analogous "template" approaches be used to grow single-crystalline films of perovskite-related ferroelectrics with controlled crystallographic orientations? In the case of the layered superconductor $YBa_2Cu_3O_{7-\delta}$, this has been shown to be possible (*7, 8*) by taking advantage of the tripled perovskite crystal structure of $YBa_2Cu_3O_{7-\delta}$. Growth at elevated temperatures leads to an epitaxial film oriented with its long (*c*) axis standing up (perpendicular to the plane of the substrate). By simply reducing the growth temperature by about 100°C, the long axis can be made to lie down (an *a* axis–oriented film) on the same cubic perovskite surface.



An example of the importance of film orientation on the piezoelectric properties of PZT.

In the case of layered bismuth-based perovskite-related ferroelectrics such as $Bi_4Ti_3O_{12}$, however, orientation control through purely thermal means has proven elusive. The difficulty arises from the additional complexity of the crystal structure. The Bi_2O_2 layers and crystallographic glide planes in these ferroelectrics destroy the in-plane lattice match between the long axis (the *c* axis) of the ferroelectric and a perovskite substrate.

One tripled-perovskite-layer segment of $Bi_4Ti_3O_{12}$ can be well lattice-matched with the perovskite substrate, but the next tripled-perovskite layer will be offset from the substrate, destroying the lattice match for $Bi_4Ti_3O_{12}$ growth with its long axis lying down (see the upper figure, B).

Thus, while it is quite easy to grow films of $Bi_4Ti_3O_{12}$ in which the long axis stands up (*c* axis–oriented films) (*4, 9*), growing *a* axis– or *b* axis–oriented films of layered bismuth-based perovskite-related ferroelectrics has been more difficult. This is especially true when growth on a bottom electrode is required for ferroelectric capacitor-type applications.

The pioneering work of Wu and colleagues (*10, 11*) demonstrated the epitaxial growth of high-quality *a* axis– and *b* axis–oriented $Bi_4Ti_3O_{12}$ films on (110) MgO and (110) $MgAl_2O_4$ substrates, but not on silicon. Because the films were grown without bottom electrodes, they had to be peeled off from the insulating substrates to make electrical measurements (*10*).

In the 30 years since then, some progress has been made in tilting the *c* axis of layered bismuth-based perovskite-related ferroelectrics and growing them on a conductive bottom electrode. Such a geometry is favored for ferroelectric capacitor applications, including memories, which require a bottom electrode for vertical measurements. For example, when the *c* axis was tilted by ~57° through epitaxial growth on a (111)-oriented conductive perovskite buffer layer, an increase in spontaneous polarization was observed (*12*). This approach was recently extended to silicon substrates (*13*). A tilt of 57°, however, is not the full 90° tilt desired for the optimization of

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the ferroelectric properties for capacitor applications.

Lee *et al.* have devised a method to tilt an epitaxial $Bi_4Ti_3O_{12}$ film on an underlying conducting bottom electrode a full 90°. The method involves using an epitaxial (001) cubic zirconia buffer layer to transition from a (001) $SrRuO_3$ film, used as the bottom electrode, to a (001) Si substrate. The crystallographic orientation in the La-doped bismuth titanate layer is controlled through the growth rate. The resulting *a* axis–oriented La-doped epitaxial bismuth titanate films are grown on a silicon substrate and have the optimal orientation for nonvolatile ferroelectric memories. This approach opens a new vista within the field of ferroelectric memories, and more generally in the area of growth of complex layered oxides on technologically relevant substrates. The ability to carefully control crystallographic orientation and therefore create a highly oriented thin film should enable development of the next-generation of ferroelectronic devices.

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PERSPECTIVES: GENOMICS AND MICROBIOLOGY

Microbial Forensics— "Cross-Examining Pathogens"

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Microbial pathogens cause disease as a result of their intrinsic adaptive strategy for replication and survival within a host. In a problematic modern world, however, microbial-related disease may also be the consequence of a forced interaction between microbe and host or manipulation of the microbe's genome by malevolent persons. In the case of both naturally occurring "emerging" infectious diseases, and disease induced by human intent (bioterrorism), it is important to establish "attribution." When explored in either a scientific or legal courtroom, the source of a pathogen, and its origins and relatedness to other strains and species, reveal mechanisms by which virulence arises and the host-microbial equilibrium becomes disrupted. In the arena of emerging microbial diseases, these critical issues are addressed with increasing frequency using molecular microbial signatures. The study of emerging infectious diseases and new pathogens (*1*), and the criminal justice system have evolved in a similar fashion: Both have shifted away from reliance on biological phenotypes of the suspected perpetrator, such as fingerprints, and toward more reliable and quantifiable molecular markers, such as polymorphisms (variations) in the DNA sequence.

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Comparative genome sequencing, in particular, offers a powerful approach for analyzing genetic variation and relatedness within and between species, and for resolving differences between two strains that superficially look identical. However, the speed of the evolutionary clock (that is, the rate of accumulation of genetic variations) for some microbial species, such as *Bacillus anthracis*, the causative organism of anthrax, is quite slow. For these organisms, the ability to discriminate between strains has been limited by the paucity of known genetic polymorphisms.

Read and co-workers from The Institute for Genomic Research (TIGR) now report on page 2028 of this issue the comprehensive identification of genetic polymorphisms in two related strains of *B. anthracis* by comparative full-genome sequencing (*2*). They compared the Porton isolate of the Ames strain with an isolate from the index case in Florida of the October 2001 mail anthrax attacks (*2*, *3*). Importantly, they introduce a statistical model that distinguishes between true genetic polymorphisms and random sequencing errors. Furthermore, the discriminating power of these polymorphism markers is demonstrated by the typing of closely related *B. anthracis* strains. Their impressive demonstration of polymorphism detection and analysis, especially in such a genetically homogeneous bacterium, is an important contribution to the molecular typing field. Their work establishes a methodology for the comprehensive identification of sequence polymorphisms and their deployment as typing markers.

Microbial forensics, as we define it, is the detection of reliably measured molecular variations between related microbial strains and their use to infer the origin, relationships, or transmission route of a particular isolate. These variations or markers include genome sequence polymorphisms, which can be detected by direct sequencing or by hybridization-based methods; genomewide patterns of gene expression, which can be easily measured with DNA microarrays; and differences in protein or small-molecule patterns, which can be detected by spectroscopic or other methods. These same techniques can be used to study population structure, species evolution, and acquisition of virulence (*4*, *5*).

The application of molecular markers in forensic studies has led to some high-profile discoveries. For example, the alleged transmission of HIV from a Florida dentist to several patients was supported by sequencing of amplified viral fragments from the dentist and the infected patients (*6*). Recently, using multiple-locus variable number tandem repeat (VNTR) analysis, the Aum Shinrikyo *B. anthracis* bioterror strain was identified as the veterinary vaccine strain, Sterne 34F2 (*7*). Although TIGR's interest in *B. anthracis* genomics predates October 2001, the choice of the Florida strain for analysis was influenced by the ensuing public health and criminal investigations. Both criminal investigation of bioterrorism attacks and studies of naturally occurring disease outbreaks will continue to be important applications of this technology. In fact, in some cases, it is difficult at the outset to distinguish mother nature from man as the perpetrator: The investigation of the West Nile virus outbreak in the northeastern United States in 1999 eventually revealed a single strain from birds and humans in New York with greatest similarity to a strain originally isolated from a dead goose in Israel, leading to the conclusion that the outbreak was of natural origin (*8*, *9*). Cultivation of an organism may not be necessary for genotyping: Random or targeted genome amplification from picogram quantities of DNA (*10*) may facilitate microbial forensic analysis of micromanipulated single cells, and direct analysis of clinical specimens.

How can we improve upon the use of polymorphic sequence markers to distinguish and establish relationships between strains reliably and unambiguously? Comparison of two strains will identify only a

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