6

Nanometer-Sized Ferroelectric Capacitors

6.1 Introduction

Ferroelectric materials possess unique dielectric, piezoelectric, pyroelectric, and electro-optic properties, which make them suitable for applications in various microelectronic and micromechanical devices (Lines and Glass 1977). Owing to the sustained trend toward the miniaturization of electronic devices, ferroelectrics are mostly used nowadays in thin-film form (Dawber et al. 2005, Setter et al. 2006). In particular, the switching of spontaneous polarization in a ferroelectric film is employed in low-power and fast nonvolatile random access memories (FeRAMs) produced for smart cards (Scott 2000, Ishiwara and Okuyama 2004, Kohlstedt et al. 2005a). Owing to their high piezoelectric and pyroelectric responses, ferroelectric thin films are promising for applications in various sensors and actuators and as the heart of microelectromechanical systems (MEMS) that combine Si-technology with the latest achievements in micromechanics (Scott 2007).

Numerous experimental and theoretical studies performed during the past decade have demonstrated that the physical properties of ferroelectric thin films may be very different from those of bulk ferroelectrics. When the film thickness or the lateral size of a ferroelectric capacitor (Figure 6.1) is reduced down to the nanoscale range, these properties generally become size-dependent. Therefore, the physics of nanoscale ferroelectrics represents an exciting field of research in solid-state physics with a close link to device applications. Impressive progress made in this field is mainly the result of the following three recent achievements: (1) new theoretical investigations based on the phenomenological Landau theory of phase transitions (Landau et al. 1984) and the ab initio calculations of ferroelectric crystals and thin films; (2) tremendous improvement in the thin-film technology of complex oxides by using sophisticated deposition techniques and patterning; and (3) the advent of advanced analytical tools. The corresponding “research triangle” is sketched in Figure 6.1.

The phenomenological theory of bulk ferroelectrics was founded in the middle of the twentieth century and proved to be very successful in describing the physical properties of these materials (Devonshire 1954, Lines and Glass 1977). However, this mean-field theory, which is usually termed the Landau–Ginzburg–Devonshire theory, cannot be directly applied to thin-film and nanoscale ferroelectrics. The presence of surfaces (interfaces) and considerable lattice strains in these material systems require significant modifications of this thermodynamic theory (Kretschmer and Binder 1979, Pertsev et al. 1998). In particular, Pertsev et al. (1998) have shown that the substrate-induced lattice strains may give rise to new polarization states and phase transitions in epitaxial ferroelectric thin films. Subsequent experimental studies of single-crystalline films grown on dissimilar substrates confirmed many of the theoretical predictions and demonstrated the importance of strain effects in ferroelectric films (Schlom et al. 2007).
In parallel to important developments in the theoretical physics of ferroelectrics, we can notice essential improvements in thin-film growth and characterization techniques. Today, these improvements allow an atomic level of control of ferroelectric inorganic materials such as BaTiO$_3$ and PbZr$_{1-x}$Ti$_x$O$_3$ (PZT) at the interfaces with lattice-matched substrates (SrTiO$_3$, NdGaO$_3$, DyScO$_3$, etc.) and electrodes made of metal oxides (SrRuO$_3$, LaSr$_2$Mn$_{1-x}$O$_3$, etc.). Molecular beam epitaxy (MBE), a sophisticated method borrowed from semiconductor technology, pulsed laser deposition, and sputtering, is the work horse in the growth of thin-film ferroelectrics. Essential progress in the structural analysis by transmission electron microscopy and the advent of nanoscale scanning probe techniques of ferroelectric thin films led to a considerable progress in the thin-film deposition, as well as in the understanding of ferroelectrics at the nanometer and angstrom scale (Gruverman and Khoklin 2004, Schlom et al. 2007, Jia et al. 2008).

In this chapter, we first briefly discuss the basic physics of ferroelectric materials and then focus on nanoscale ferroelectric capacitors and future prospects in this research area. Because of the length limit, we restrict our discussion to the class of inorganic ferroelectrics and related devices. Readers interested in ferroelectric polymers, ferroelectric liquid crystals, and ferroelectric II–VI mixed compounds are referred to the relevant publications (Weil et al. 1989, Xu 1991).

This chapter is organized in the following way. In Section 6.2, the fundamentals of ferroelectricity are presented. Section 6.3 is devoted to the state-of-the-art deposition and patterning techniques, whereas Section 6.4 describes the various aspects of the structural and electrical characterization of ferroelectric thin films and capacitors. In Section 6.5, the most important physical phenomena occurring in ferroelectric capacitors are discussed. New developments and emerging trends in the field of nanoscale ferroelectric devices are briefly described in Section 6.6.

### 6.2 Fundamentals of Ferroelectricity

Ferroelectricity was discovered by J. Valasek in Rochelle salt in 1920 (Valasek 1921). The phenomenological definition of ferroelectricity in the textbook by Lines and Class reads: "A crystal is said to be ferroelectric material when it has two or more orientational states in the absence of an electric field. Any two of the orientation states are identical (or enantiomorphous) in crystal structure and differ only in electric polarization vector at null electric field" (Lines and Glass 1977). The crystal symmetry imposes restrictions on the existence of the spontaneous polarization $P_s$. First, this property is not allowed in the presence of a center of symmetry, which excludes 11 centro symmetric groups from the total set of 32 crystallographic point groups. Second, only 10 point groups out of the remaining 21 noncentrosymmetric ones posses a polar axis along which the spontaneous polarization may develop. This subset corresponds to
pyroelectric crystals, where the build-in polarization manifests itself in temperature-induced changes of the total dipole moment of the unit cell. Ferroelectrics represents a subclass of pyroelectric crystals: they are distinguished from other pyroelectric materials by their ability to switch between two or more stable states with different spontaneous polarization under the action of sufficiently strong external electric field. Indeed, this switching field must be lower than the breakdown field of the material.

Currently, about 700 ferroelectric materials are known (Scott 2007), which can be divided into several groups in accordance with the microscopic origin of ferroelectricity and their atomic structure. The most important examples are ferroelectric oxides such as BaTiO$_3$ and SrBi$_2$Ta$_2$O$_9$, hydrogen-bonded ferroelectrics (e.g., KH$_2$PO$_4$), ferroelectric polymers like poly(vinylidenefluoride), and ferroelectric liquid crystals (Lines and Glass 1977, Xu 1991). There are many industrial applications of ferroelectric materials, ranging from BaTiO$_3$ capacitors to ferroelectric-liquid-crystal displays for flat TV screens.

In this chapter, we focus on ferroelectric oxides with the perovskite structure, i.e., with the crystal structure characteristic of the mineral CaTiO$_3$ found in the Ural Mountains and named "perovskite." The general chemical formula for perovskite oxides is ABO$_3$, where A and B represent two cations of very different sizes. In the cubic unit cell of a perovskite oxide, the A-type atoms are situated at the cube corners, the B-type atom sits at the cube center, and oxygen atoms are located at the face centers. In Figure 6.2, the unit cell of the perovskite oxide BaTiO$_3$ is shown schematically for the cubic and tetragonal phases. In the high-temperature cubic state, BaTiO$_3$ is indeed paraelectric with a zero dipole moment of the unit cell. Below about 120°C, stress-free bulk crystals of BaTiO$_3$ become ferroelectric owing to a small shift of the Ti$^{4+}$ ion relative to the center of the surrounding oxygen cage, which leads to the appearance of dipole moment and lattice spontaneous polarization. Since the direction of this shift depends on temperature $T$, BaTiO$_3$ has three different ferroelectric phases: tetragonal ($10°C ≤ T ≤ 120°C$), orthorhombic ($−71°C ≤ T ≤ 10°C$), and rhombohedral ($T ≤ −71°C$) (Jona and Shirane 1962).

The build-in switchable polarization $P$ represents the most important physical characteristic of a ferroelectric material. In the thermodynamic theory of ferroelectrics, the polarization vector $P$ is used as an order parameter and the additional Gibbs free energy density $\Delta G(P)$ of the ferroelectric phase is expanded in terms of the polarization components $P_i$ ($i = 1$, 2, 3). For a stress-free tetragonal ferroelectric crystal subjected to an electric field $E$ parallel to the polar $x_3$ axis ($P_z = P_e = 0$, $P_x ≠ 0$), the Gibbs free energy $G_\text{ferro}$ can be written as

$$G_\text{ferro} = G_{\text{para}} + a_1P_1^2 + a_{11}P_3^4 + \cdots - P_xE_3,$$

where $a_1$, $a_{11}$, and $a_{111}$ are the dielectric stiffness and higher-order stiffness coefficients of the centrosymmetric paraelectric phase at constant stress. The dielectric stiffness $a_1$ is given the linear temperature dependence $a_1 = (T − \theta)/(2ε_0C)$, where $\theta$ and $C$ are the Curie–Weiss temperature and constant and $ε_0$ is the permittivity of the vacuum. The minimization of $\Delta G(P)$ makes it possible to calculate the polarization $P_x$ of a homogeneously polarized crystal as a function of temperature $T$ and applied field $E_3$. When the coefficient $a_{11}$ of the fourth-order polarization term is positive, the spontaneous polarization $P_x = P_0 (E_3 = 0)$ remains zero down to the transition temperature $T_c = \theta$, below which it increases gradually as $P_x \sim \sqrt{T_c − T}$. The energetics of this second-order ferroelectric phase transition is described schematically in Figure 6.3b. In contrast, at $a_{11} < 0$ and $a_{111} > 0$, the spontaneous polarization displays a step-like increase up to a value of $P_x = \sqrt{a_{11}/2a_{111}}$ at $T_c = \theta + \epsilon_0C a_{111}/(2a_{111})$. Therefore, a first-order ferroelectric phase transition takes place in this situation, as illustrated in Figure 6.3a.

Under an external field directed against the spontaneous polarization, the magnitude of $P_x(E_3)$ first gradually decreases with increasing field intensity $E_3$. When it reduces down to a certain minimum value $P_{\text{min}}$, the "antiparallel" polarization state becomes unstable. As a result, the polarization switches by 180° into the direction parallel to the applied field. In the case of ferroelectrics with a second-order transition, $P_{\text{min}} = P/\sqrt{3}$, and the critical switching field equals $E_{3_c} = (4/3)a_{111}P_{\text{min}} (T_c − T)^{-1/2}$. The field $E_{3_c}$ represents the thermodynamic coercive field that corresponds to a homogeneous polarization reversal in the whole crystal. The polarization-field curve resulting from the thermodynamic calculations is hysteretic, as shown in Figure 6.4a. The theoretical hysteresis loop is qualitatively similar to the experimental ones, which differ mainly by a gradual polarization.

**FIGURE 6.2** Schematic representation of the unit cell of BaTiO$_3$ in the paraelectric cubic (a) and ferroelectric tetragonal (b) phases.

**FIGURE 6.3** Temperature evolution of the free energy density as a function of polarization shown schematically for ferroelectrics with the first-order (a) and second-order (b) phase transition.
reversal seen in Figure 6.4b. The measured coercive fields $E_c$ of bulk crystals, however, are typically several orders of magnitude lower than $E_{th}$ because the polarization switching develops in reality via the nucleation and growth of ferroelectric domains (Lines and Glass 1977).

When the size of a ferroelectric crystal is reduced down to a length scale comparable to the so-called ferroelectric correlation length, its physical properties generally become size-dependent. This feature is due to the fact that ferroelectricity is a collective phenomenon resulting from a delicate balance between long-range Coulomb forces (dipole–dipole interactions), which are responsible for the ferroelectric state, and a short-range repulsion favoring the paraelectric state (Lines and Glass 1977).

The scaling of physical characteristics such as the remanent mean polarization $P_r = \langle P_z(E_z = 0) \rangle$ and coercive field $E_c$ is currently in the focus of experimental and theoretical studies in the field of nanometer-sized ferroelectric capacitors. The most important results of these studies will be discussed in Sections 6.4 and 6.5.

### 6.3 Deposition and Patterning

#### 6.3.1 General Aspects

The deposition of thin films belongs to the heart of today’s micro- and nano-electronics. In order to grow thin films with desired properties, several important issues have to be considered. Besides the choice of the deposition method, a number of process parameters are essential, such as the background pressure of the vacuum system, the deposition rate (measured in nm/s), the substrate material and temperature, and the composition of the material source. Furthermore, the process pressure is important, irrespective of the conditions in the chamber, i.e., the state of an ultra-high vacuum or the presence of a noble gas (typically argon) or reactive gases (oxygen or nitrogen). The basic principles of thin-film deposition are described in several textbooks (Chopra 1969, Maisel and Glang 1979, Bunshah 1994).

Here we focus on the deposition of complex oxides by means of physical methods.

As already mentioned in the introduction, thin-film deposition techniques for the growth of heteroepitaxial oxides have made tremendous progress recently. The purpose of this section is to give a short overview of the current status of the MBE, pulsed laser deposition (PLD), and sputter deposition (SD). For chemical-based methods, such as metal-organic chemical vapor deposition (MOCVD), atomic layer deposition (ALD), and chemical solution deposition (CSD), we refer the reader to the relevant papers (Oikawa et al. 2004, Kato et al. 2007, Schneller and Waser 2007). We also note that ferroelectric polymers are deposited by either a spin-on technique or the Langmuir-Blodgett method (Ducharme et al. 2002).

Consider a planar ferroelectric capacitor sketched in Figure 6.1. The choice of materials for the substrate, electrodes, and ferroelectric layer strongly depends on the application or the research task. For the epitaxial growth of perovskite ferroelectrics, single-crystalline substrates having small lattice mismatches with these complex oxides are preferable. At present, the commercially available single crystals of SrTiO$_3$ are most popular, although other substrates such as MgO, KTaO$_3$, GdScO$_3$, and DyScO$_3$ have also been successfully employed. When the ferroelectric overlayer is commensurate with a dissimilar thick substrate, it appears to be strained to a certain extent defined by the mismatch in their in-plane lattice parameters. Above some critical thickness, however, these lattice strains start to relax due to the generation of misfit dislocations (see Section 6.4).

As for the electrodes, noble metals such as Pt, Ir (also IrO$_2$), and Ru are used in most device applications, e.g., in FerAMs and MEMS (Kohlstedt et al. 2005a). On the contrary, conducting complex oxides were favored so far as electrode materials in the basic research studies of scaling effects. Prominent examples of such electrode materials are SrRuO$_3$, LaSr$_{m-x}$Mn$_x$O$_3$, and LaCa$_{m-x}$Mn$_x$O$_3$, which are routinely used in the complex-oxide heterostructures (Eom et al. 1992, Sun 1998). A comparison of the advantages and disadvantages of metal and oxide electrodes shows a delicate trade-off. Let us compare, for instance, Pt and SrRuO$_3$.

![Theoretical (a) and measured (b) ferroelectric hysteresis loops.](image-url)
On the one hand, the resistivity of a sputtered thin-film Pt at room temperature (≈10 μΩ cm) is much smaller than that of even a high-quality SrRuO$_3$ (≈300 μΩ cm). On the other hand, the screening-space-charge capacitance density, which is important for the stabilization of ferroelectricity in ultrathin films (Pertsev and Kohlstedt 2007), is equal to 0.9 F/m$^2$ for the SrRuO$_3$ electrode and only to 0.4 F/m$^2$ for the Pt electrode (Pertsev et al. 2007). This feature seems to make SrRuO$_3$ electrodes preferable for nanoscale ferroelectric capacitors. In addition, the electrode surface roughness, crystallographic orientation of the ferroelectric layer grown on a particular electrode, and the quality of the electrode–ferroelectric interface must be taken into account. Currently, conducting complex oxides are preferred for the fabrication of the bottom electrode, whereas the top electrode can be made of Pt or other noble metal as well. In the rest of this section, we focus on entirely complex-oxide heterostructures for ferroelectric capacitors.

### 6.3.2 Deposition Techniques

#### 6.3.2.1 Molecular Beam Epitaxy (MBE)

MBE has developed from a simple evaporation technique via the use of ultra-high vacuum (UHV) to avoid disturbances by residual gases and additional incorporation of various effusion (Knudson) cells as material sources. Figure 6.5 schematically shows an MBE system involving several material sources that allow controlled deposition of multi-element compounds. In contrast to the deposition of most semiconductor materials such as GaN, GaAs, and InP, the growth of oxides by MBE requires relatively high partial pressure of oxygen (≈10$^{-7}$ mbar) during the deposition. This is necessary to avoid the oxygen deficiency in the final film, which could seriously deteriorate the quality of a ferroelectric capacitor. Partial pumping, the use of reactive oxygen (e.g., ozone), and post-annealing of the films in a high-pressure oxygen atmosphere (several mbar) are used to supply the films with a sufficient amount of oxygen.

Owing to the UHV conditions in the MBE chamber, all UHV surface techniques can be employed. This feature, indeed, constitutes the strength of MBE (Haeni et al. 2000). This tool offers the highest degree of freedom to apply sophisticated in situ analytical techniques to study films during the growth and just after the deposition without breaking the vacuum. Complex MBE systems using low-energy electron microscopy (LEEM) and Auger electron spectroscopy (AES), for example, were developed (Habermeier 2007 and Clayhold et al. 2008). The standard technique currently is the reflection high-energy electron diffraction (RHEED), which allows control of the surface chemistry of the last layer during the deposition. This technique provides an opportunity to fabricate oxide films with a definite termination at the surface (e.g., the BaO or TiO$_2$ termination in BaTiO$_3$ films). Many groups successfully demonstrated this approach (Logvenov and Bozovic 2008) with similar oxide materials. An obvious research goal now is to find correlations between atomic terminations at ferroelectric–metal interfaces and the electrical properties of capacitors.

![MBE System Diagram](image.png)

**FIGURE 6.5** Schematic view of MBE system for the growth of multi-element-compound thin films (a) and a photograph of MBE chamber (b). (From Lettieri, J. et al., *J. Vac. Sci. Technol. A*, 20, 1332, 2002. With permission.)
An additional important feature of MBE is the low energy of deposited species. Indeed, the temperature of the material source in effusion cells or electron-beam evaporators does not exceed 3500 K. Hence, the corresponding thermal energy of the deposited species is about 300 meV. This value is an order of magnitude lower than the energies characterizing pulsed laser deposition and typical sputter deposition. Among available deposition techniques, MBE is the most flexible one with respect to the incorporation of analytical tools and offers the highest degree of atomic layer control. On the other hand, MBE systems are difficult to handle, considerable time is necessary for their maintenance, and, last but not least, special methods are needed to supply complex oxides with a sufficient amount of oxygen. Due to the highly complex machinery, experienced researchers working with MBE systems for years translated the acronym MBE as “many boring evenings.”

6.3.2.2 Pulsed Laser Deposition

PLD is a very useful and flexible tool for growing oxide materials (Hubler and Chrisey 1994). A sketch of a PLD system is shown in Figure 6.6. A pulsed laser beam, from a KrF (248 nm) or ArF (193 nm) excimer laser, for example, is focused on a rotating target made of an oxide material (e.g., BaTiO$_3$, PZT, or SrRuO$_3$). The oxygen gas pressure during ablation can be varied from $10^{-7}$ to 0.5 mbar. Owing to the intense laser beam, a plasma containing energetic ions, electrons, neutral atoms, and molecules is formed. The energy density is in the range of 2–5 J/cm$^2$ at the target surface. As a result, the energy of the ablated material may reach values of 10 eV at the substrate surface. The wavelength of the used laser beam may be 248 or 193 nm (at this UV wavelength, the absorption in the oxide target materials is sufficiently large).

A repetition rate of several Hz and a pulse length of 25 ns represent typical parameters. Initially, a serious problem of the method was the formation of droplets on the substrate, which can easily deteriorate the device properties. Currently, various methods to reduce this effect are known, e.g., the time-of-flight selection of ablated material. PLD systems are widely used for basic research studies of thin films. The main advantage of this method is that a certain film stoichiometry can be easily achieved by PLD. Many targets (six or more) can be placed on the target carousel holder. In this way, numerous materials can be deposited without time-consuming rearrangements of the deposition chamber or complicated source exchange procedures, as in the case of MBE or MOCVD.

6.3.2.3 Sputter Deposition

Plasma sputtering is a physical vapor deposition technique that has been known for 150 years since the time when W.R. Grove first observed the sputtering of surface atoms. Different sputtering techniques, such as dc- and rf-sputtering with or without a magnetron arrangement, have been used to grow a variety of materials. Figure 6.7a illustrates the principle of dc-sputtering. A potential of several hundred volts is applied between the target (cathode) and the heater (anode), accelerating positively charged ions toward the target. These accelerated particles sputter off the target material, which finally arrives at the substrate. The discharge is maintained because the accelerated electrons continuously collide with the gas circulating in the chamber and ionize new atoms.

For insulating targets such as ferroelectric ones, the dc-sputtering is not suitable. Insulating targets have to be sputtered using alternating electric fields to generate the plasma. Typically, an rf-frequency of 13.56 MHz is employed. This frequency is not a magic number, rather a frequency that is approved by the government for industrial purposes. A symmetrical arrangement of cathode and anode and the use of a low-frequency alternating field would result in similar sputtering and re-sputtering rates so that the film will not grow. In the case of a high-frequency alternating field, however, light electrons can respond to the field at this frequency, whereas heavy Ar$^+$ ions see only an average electric field (Kawamura et al. 1999). Moreover, the geometrical asymmetry between small cathodes (target side) and large anodes (heater and chamber) leads to a higher electron concentration at the former, resulting in a self-generated dc bias that accelerates Ar$^+$ ions toward the target.

The high-pressure sputtering technique of oxide materials was developed by Poppe et al. (1988) and served initially for the
growth of oxide superconductors. A planar on-axis arrangement of the target and substrate is used, as shown in Figure 6.7b. A high sputtering pressure of 2.5–3.5 mbar, corresponding to a mean-free-path \( \lambda_{\text{mean free}} = 6 \times 10^{-3} \text{ cm at } 600^\circ \text{C} \) and exceeding largely the pressure of \( 10^{-2} \text{ mbar} \) used for conventional sputtering (\( \lambda_{\text{mean free}} = 2 \text{ cm at } 600^\circ \text{C} \)), leads to multiple scattering of the negatively charged oxygen ions accelerated toward the substrate. As a result of the thermalization of ions, the re-sputtering of the deposited films, which is caused by negatively charged ions, is negligible. This technique yields excellent thin films due to the low kinetic energy (as in the case of MBE) of sputtered particles.

A disadvantage of the high-pressure sputtering technique could be a low deposition rate of several nanometers per hour, which may lead to interdiffusion at heterogeneous interfaces. To enhance the deposition rate, a low ionization degree of less than 1% of the atoms in the plasma is increased by the use of magnetic fields forcing electrons onto helical paths close to the cathode, which leads to much higher ionization probability. This so-called magnetron sputtering can be employed for high-pressure sputtering (Poppe et al. 1988), as well as for conventional, low-pressure sputtering (Fisher et al. 1994). Sputtering is routinely used as a vapor deposition method for the growth of complex-oxide films.

6.3.3 Patterning

The patterning of oxide heterostructures represents an important step in the fabrication of ferroelectric capacitors with small lateral dimensions ranging from a few micrometers to tens of nanometers. As in many other areas of nano-electronics, two different approaches exist for the device fabrication. A conventional approach relies on the well-established processes used in the modern semiconductor industry: deposition, lithography, and etching. Using these techniques sequentially, ferroelectric capacitors can be fabricated. It should be emphasized that this fabrication procedure employs the so-called top-down approach, where external tools are used to create a nanoscale device out of a larger structure. In contrast, the bottom-up approach is based on the self-organization of constituents or their positional assembly necessary for a desired nanodevice. Such techniques recently became very fashionable (Spatz et al. 2000) because they do not require advanced and expensive patterning tools. The bottom-up approach has had considerable success, but improvements are needed to achieve registered arrays of devices, such as those produced by the state-of-the-art complementary metal-oxide-semiconductor (CMOS) technology. In some works, mixed top-down and bottom-up methods were used to produce nanoscale ferroelectric dots and crystals (Kronholz et al. 2006, Szafraniak et al. 2008).

One of the simplest ways to fabricate ferroelectric capacitors is the lift-off technique. The main steps of this technique are shown in Figure 6.8a. First, the bottom electrode and the ferroelectric layer are deposited on a substrate. A subsequent photo-lithographic step defines the area of the capacitor. Next, the top electrode is deposited, for example, by the sputtering of Pt. After a lift-off in acetone, the metal with photoresist underneath is removed and the capacitor is ready for electrical characterization. Because the top interface is subjected to photore sist and chemical developer during this procedure, relatively poor electrical properties (e.g., large leakage) are observed here (Rodríguez et al. 2003a and Rodríguez Contreras 2004). The post-annealing of capacitors at high temperatures and in an oxygen atmosphere was successfully used to improve the electrical properties considerably (Schneller and Waser 2007).

The aforementioned drawback, however, can be avoided using another method, which involves the fabrication steps shown schematically in Figure 6.8b. Here the whole sandwich (bottom...
6.4 Characterization of Ferroelectric Films and Capacitors

6.4.1 Rutherford Backscattering Spectrometry

Rutherford backscattering spectrometry (RBS) is an accurate nondestructive technique for measuring the stoichiometry, layer thickness, quality of interfaces, and crystalline perfection of thin films. RBS offers a quantitative determination of the absolute concentrations of different elements in multi-elemental thin films. A collimated mono-energetic beam of low-mass ions hits the specimen to be analyzed. Typically, He\(^+\) ions with energy of 1.4 MeV are used in RBS experiments. A small fraction of the ions that impinge on the sample is scattered back elastically by the atomic nuclei and are then collected by a detector. The detector determines the energy of the backscattered ions, which provides an RBS energy spectrum. The RBS spectra describe the yield of backscattered particles as a function of their energy. The analysis of RBS spectra is done using modern software. A more detailed description of the technique is given by Chu et al. (1978).

In the so-called random experiments, the ion beam is not aligned with respect to the crystallographic directions of the specimen. The energy distribution of the collected ions provides information on the masses of atoms constituting the sample and on the thicknesses of deposited layers. Information on the sharpness of interfaces between these layers is given by the abruptness of the low-energy edge in the “random” spectrum.

Epitaxial films usually have the same major channeling axis as the substrate. The degree of epitaxy is determined from ion channeling experiments by a ratio of the elemental signals from the film for the channeled and random sample orientations. This ratio is called the “minimum yield,” \(\chi_{\text{min}}\), and its value provides information on the crystalline perfection of a film. Defects inside the film lead to higher values of \(\chi_{\text{min}}\).

6.4.2 X-Ray Diffraction for Thin-Film Analysis

X-ray diffraction (XRD) represents a powerful tool for the characterization of thin films. It can be used to determine whether...
the film grown on a crystalline substrate is amorphous, polycrystalline, or single-crystalline (epitaxial growth). Moreover, this technique makes it possible to determine the film thickness, lattice parameters, and the amount of strain in an epitaxially grown film with a high precision.

In particular, the 2θ scans performed at a fixed glancing incident angle of the incoming x-ray beam (in the range of 0.5°–2°) are suited for the investigations of polycrystalline films, since the spectrum contains only the peaks coming from the XRD of randomly oriented crystallites. (The single-crystal substrate does not contribute to the XRD because the Bragg condition is not satisfied for this angle of incidence.) For (001)-oriented epitaxial films, the normal θ–2θ scans reveal only the (00l) reflections. Thus, we can distinguish between an epitaxial film on a crystalline substrate and a polycrystalline one. Moreover, from the 2θ position of these reflections, one can precisely determine the out-of-plane lattice parameter. Once this parameter is measured, the in-plane lattice constants could be determined as well by finding the peak positions of the (h0l) reflections, for example. For ultrathin films, however, this becomes difficult because of the overlap with substrate peaks. Therefore, the grazing incidence diffraction, which is characterized by a low penetration depth of the incoming x-ray beam, has to be used to measure the in-plane lattice constants of ultrathin films.

The amount of strain in an epitaxial film can be nicely visualized by the reciprocal space maps measured, for example, around an asymmetric (013) reflection. These maps can indicate whether the film is fully strained by the substrate or is partially relaxed owing to the generation of misfit dislocations. Representative reciprocal space maps of strained and relaxed epitaxial BaTiO$_3$ films grown on SrRuO$_3$-covered SrTiO$_3$ substrates are given in Figure 6.10a and b. The out-of-plane and in-plane lattice parameters of BaTiO$_3$ films extracted from such maps are plotted in Figure 6.10c as a function of the film thickness $t$ (Petraru et al. 2007). It can be seen that ultrathin films with $t < 30$ nm are commensurate with the substrate, which results in a compressive biaxial in-plane strain and an out-of-plane elongation of the unit cell.

The synchrotron x-ray scattering measurements give additional possibilities for the characterization of ultrathin films (Fong et al. 2005). In particular, it was demonstrated that electrode-free PbTiO$_3$ films grown on SrTiO$_3$ remain ferroelectric for thicknesses down to only 3 unit cells (Fong et al. 2004).

Finally, we note that the film thickness itself can be measured precisely using the x-ray specular reflectivity method based on interference fringes whose spacing is characteristic for this thickness (Fewster 1996). This method can be applied to films with any structure, crystalline or amorphous, but requires a flat surface over the region studied. It was demonstrated to work even

![FIGURE 6.10 X-ray reciprocal space maps around the (103) Bragg reflection obtained for fully strained (a) and partially relaxed (b) BaTiO$_3$ films epitaxially grown on SrRuO$_3$-covered SrTiO$_3$. The film lattice parameters are plotted as a function of the film thickness in panel (c). (From Petraru, A. et al., J. Appl. Phys., 101, 114106, 2007. With permission.)](image)
6.4.3 Ferroelectric Capacitors: P-E Hysteresis Loop Measurements

A ferroelectric capacitor usually displays a polarization-field (P-E) hysteresis loop similar to that shown in Figure 6.4b. There are several techniques that are used to measure the P-E loops of ferroelectric capacitors. The simplest method employs a circuit proposed by Sawyer and Tower, which is shown schematically in Figure 6.12a. The circuit consists of a fixed capacitor with known capacitance, the test ferroelectric capacitor, an oscilloscope, and a function generator. The method relies on the fact that two capacitors in a series have the same charge. The ac voltage created by the generator and the potential across the standard capacitor are shown on the x- and y-axes of the oscilloscope. The capacitance of the standard capacitor is chosen to be large enough so that the voltage drop across this capacitor is much smaller than the potential difference across the tested ferroelectric capacitor.

Another method uses a fast current-to-voltage converter connected in series with the ferroelectric capacitor (see the circuit shown in Figure 6.12b). In this case, the current-voltage curve is measured as a response of the ferroelectric capacitor to a triangular signal excitation. It is very useful to look at the switching current peaks that appear in this curve in order to distinguish the ferroelectric switching from artifacts, especially in the case of leaky ferroelectric samples. By numerical integration of the current over the time, the classical P-E hysteresis loop is obtained, from which the remanent polarization and the coercive field can be determined. The remanent polarization of nanoscale SrRuO$_3$/BaTiO$_3$/SrRuO$_3$ capacitors fabricated on the SrTiO$_3$ substrate is shown in Figure 6.13 as a function of the BaTiO$_3$ thickness $t$ (Petraru et al. 2008). Remarkably, even at $t = 3.5$ nm, the strained BaTiO$_3$ film

in the case of ultrathin films with thicknesses down to 24 Å. The amplitude of oscillations depends mainly on the density contrast between the layers, and the number of oscillations correlates with the roughness of the surface and interfaces involved. In the case of rough surfaces, the average intensity of reflectivity decreases rapidly with an increasing 20 angle (Nevot and Croce 1980). For epitaxial films, high-angle finite-size oscillations occurring in the 0–20 scans around the (001) peak allow determination of the number of planes involved in the diffraction, and, therefore, of the film thickness (Schuller 1980). Examples of the low- and high-angle finite-size oscillations are given in Figure 6.11.

**FIGURE 6.11** (a) Interference fringes appearing in an x-ray specular reflectivity scan for the 27 nm thick LaNiO$_3$ film deposited on SrTiO$_3$. The film thickness was calculated from the spacing of these fringes. (b) High-angle finite-size oscillations occurring in the 0–20 scan around the (001) peak of the BaTiO$_3$ film (7.5 nm thick) grown on SrRuO$_3$-covered SrTiO$_3$. The solid line shows the measured signal, whereas the dots denote the results of simulations.
remains ferroelectric and has a remanent polarization larger than the spontaneous polarization $P_r = 26 \mu C/cm^2$ of bulk BaTiO$_3$. The coercive field $E_c$ of BaTiO$_3$ capacitors relatively weakly depends on the thickness $t$ (Jo et al. 2006b), which contrasts with a strong increase of $E_c$ (Figure 6.14) in ultrathin PZT capacitors with Pt top electrodes (Pertsev et al. 2003b).

Ferroelectric capacitors are often rather leaky, because thin films, especially at small thicknesses, are not perfect insulators. The conduction here results from the Schottky injection or Fowler–Nordheim tunneling through the interfacial barrier followed by the charge transport across the film via the Poole–Frenkel conduction mechanism, space-charge-limited conduction, or variable range hopping (Dawber et al. 2005). The leakage contribution to the total current can be singled out with the aid of the positive-up negative-down (PUND) pulsed method (Smolenskii et al. 1984). It involves the application of a series of voltage pulses from a function generator and the measurement of the transient current response of a ferroelectric device, which allows the separation of different contributions. As a representative example, we consider the sequence of five train pulses shown in Figure 6.15. The first one (0) is the pre-polarization pulse—it puts the sample into a definite polarization state. The pulse (1) switches the polarization of the sample, and its current response is the sum of the ferroelectric displacement current caused by the switching of spontaneous polarization, the dielectric displacement current, and the leakage current. The pulse (2) has the same polarity but comes after a certain delay time. Therefore, in case of a stable polarization, the current response contains only the components arising from the dielectric response and leakage current. In order to find the switchable polarization (the quantity of primary interest), the current response due to pulse (2) is subtracted from the current created by pulse (1), and the result is numerically integrated over the measuring time. Moreover, this method makes it possible to study the stability of ferroelectric polarization against back-switching. To that end, we can vary the delay time between pulses (1) and (2) and determine the relaxation time of the polarization. A similar analysis can be done for currents resulting from pulses (3) and (4) applied to the capacitor with opposite polarization.

### 6.4.4 Scanning Probe Techniques: Atomic Force Microscopy and Piezoresponse Force Microscopy

Atomic force microscopy (AFM) is one of the most widely used scanning probe microscopy (SPM) techniques (Garcia and Perez 2002). The primary purpose of an AFM instrument is to quantitatively measure the roughness of various surfaces. The lateral and vertical resolutions are typically about 5 and 0.01 nm, respectively. An atomically sharp tip is scanned over a surface with feedback mechanisms that enable the piezoelectric scanners to maintain the tip at a constant force (to obtain height information) or height (to obtain force information) above the sample surface.

Tips are typically made of Si$_3$N$_4$ or Si and extend down from the end of a cantilever. The AFM head employs an optical

![Figure 6.13](image1.png) Thickness dependence of remanent polarization in the SrRuO$_3$/BaTiO$_3$/SrRuO$_3$ ferroelectric capacitors measured at 77 K. (From Petraru, A. et al., Appl. Phys. Lett., 93, 072902, 2008. With permission.)

![Figure 6.14](image2.png) Coercive field of PZT 52/48 epitaxial films measured at 20 kHz and plotted versus the film thickness $t$ (a) and the inverse of film thickness $1/t$ (b). The straight line in (b) shows a linear fit to the experimental data, whereas the curve in (a) is a guide to the eyes.
FIGURE 6.15 Measurements of switchable ferroelectric polarization by the PUND pulsed method. The excitation signal consists of five pulses denoted by thin lines, and the current response is shown by a thick line. The upper inset demonstrates the switching (1) and nonswitching (2) current responses. The integration of their difference gives the switchable polarization plotted in the lower inset.

detection system, in which the tip is attached to the bottom of a reflective cantilever. A laser diode is focused onto the back of this cantilever. As the tip scans the surface of a sample, the laser beam is deflected by the cantilever into a four-quadrant photodiode. In contact mode, feedback from the photodiode difference signal, through the software control from a computer, enables the tip to maintain either a constant force or a constant height above the sample. In the constant force mode, the piezoelectric transducer monitors real-time height variations. In the constant height mode, the deflection force acting on the tip is recorded. The instrument gives a topographical map of the sample surface by plotting the local sample height versus the horizontal probe tip position. For many soft materials like polymers and biological samples, the operation in contact mode often modifies or destroys the surface. These complications can be avoided using the tapping-mode AFM. In tapping mode, the AFM tip–cantilever assembly oscillates at the sample surface during the scanning. As a result, the tip lightly taps the surface while scanning and only touches the sample at the bottom of each oscillation. This prevents damage of soft specimens and avoids the “pushing” of specimens along the substrate. By using a constant oscillation amplitude, a constant tip–sample distance is maintained until the scan is complete. Tapping-mode AFM can be performed on both wet and dry surfaces.

Scanning probe microscopy techniques also offer several different possibilities for the investigation of domain patterns in crystals. For imaging domain structures in ferroelectrics, piezoresponse force microscopy (PFM) is most widely used nowadays (Figure 6.16). Introduced in 1992 by Güthner and Dransfeld (1992), the PFM method has been developed by several groups to visualize domain structures in ferroelectric thin films. It became a popular tool in the science and technology of ferroelectrics and is considered to be a main instrument for getting information on ferroelectric properties at the nanoscale. Several reviews on the SPM-based methods for the characterization of ferroelectric domains are available in the literature (Gruverman and Khoklin 2004, Khoklin et al. 2007).

Ideally, when a modulation voltage \( V \) is applied to a piezoelectric material, the vertical displacement of the probing tip, which is in mechanical contact with the sample, accurately follows the motion of the sample surface resulting from the converse piezoelectric effect. The applied voltage \( V \) generates an electric field \( \mathbf{E}(\mathbf{r}) \) in the ferroelectric film, which creates the lattice strain \( \delta u_i = d_{ij}E_j \) in the film thickness direction. Here, \( d_{ij} \) are the local piezoelectric coefficients of the ferroelectric material, which depend on the polarization orientation. The strain field \( \delta u_i(\mathbf{r}) \) changes the film thickness at the tip position by an amount \( \delta \) so that the local piezoresponse signal proportional to \( \delta t/V \) can be recorded. The amplitude of the tip vibration measured by the lock-in technique provides information on the effective piezoelectric coefficient \( d_{33}^{eff} = \delta t/V \). The phase yields information on the polarization direction in a studied ferroelectric domain (Rodriguez et al. 2002). It should be noted that not only the surface electromechanical response but also the electrostatic forces could contribute to the measured signal in the PFM setup, which complicates the analysis of the PFM results. In particular, there exists a nonlocal contribution caused by the capacitive cantilever–sample interaction (Kalinin and Bonnell 2002).

Most PFM measurements are performed in a local-excitation configuration where the modulation voltage is applied between the bottom electrode and conductive SPM tip, which scans the bare surface of the film having no top electrode. In this case, the PFM image has a lateral resolution of about 10 nm (Gruverman et al. 1998). It should be noted that the electric field generated by the SPM tip in such film is highly inhomogeneous, which makes the quantitative analysis of the field-induced signal extremely difficult. In other words, PFM measurements on a sample
without extended top electrodes collect signals from a subsurface layer of unknown thickness that is a function of dielectric permittivity and contact conditions (Gruverman et al. 1998).

Alternatively, a ferroelectric film with a deposited top electrode may be studied at the expense of a lower lateral resolution. By applying a voltage to the SPM tip contacting the top electrode, a submicron variation of piezoelectric properties in PZT capacitors was demonstrated (Christman et al. 2000, Setter et al. 2006). Under these conditions, a homogeneous electric field is generated in a ferroelectric layer, and the electrostatic tip–sample interaction is suppressed. This approach allows the investigations of domain-wall dynamics and polarization reversal mechanisms in ferroelectric capacitors and quantitative studies of the scaling of piezoelectric properties in ultrathin ferroelectric films. In particular, it was found (Nagarajan et al. 2006) that the piezoelectric coefficient $d_{33}$ of epitaxial PbZr$_{0.2}$Ti$_{0.8}$O$_3$ films sandwiched between SrRuO$_3$ electrodes decreases rapidly as the thickness is reduced from 20 to 5 nm (see Figure 6.17).

### 6.5 Physical Phenomena in Ferroelectric Capacitors

There are several physical effects that make the phase states and electric properties of thin-film ferroelectric capacitors different from those of bulk ferroelectrics. First, the ferroelectric film is generally subjected to an in-plane straining and clamping due to the presence of a dissimilar thick substrate. Second, an internal electric field exists in the capacitor, which depends on the electrode material and the film thickness. Third, the scaling of
physical properties may result from the short-range interatomic interactions at the film–electrode interfaces. The current status of the theoretical description of these effects in thin films of perovskite ferroelectrics is given below.

### 6.5.1 Strain Effect

Owing to the electrostrictive coupling between lattice strains and polarization, the mechanical film–substrate interaction may strongly affect the physical properties of ferroelectric thin films (Pertsev et al. 1998). In a film deposited on a dissimilar thick substrate, the in-plane strains $u_1$, $u_2$, and $u_3$ are totally governed by the substrate, whereas the stresses $\sigma_1$, $\sigma_2$, and $\sigma_3$ are usually equal to zero. (We use the Voigt matrix notation and the reference frame with the $x_3$ axis orthogonal to the film surfaces.) Under such “mixed” mechanical boundary conditions, the equilibrium polarization state corresponds to a minimum of the modified thermodynamic potential $\tilde{G}$ (Pertsev et al. 1998), but not of the standard elastic Gibbs function $G$ (Haun et al. 1987).

In the most important case of a film grown in the (001)-oriented cubic paraelectric phase on a (001)-oriented cubic substrate ($u_1 = u_2 = u_{nm} = 0$), the stability ranges of different polarization states can be conveniently described with the aid of two-dimensional phase diagrams, where the misfit strain $u_m = (b - a_0)/a_0$ and temperature $T$ are used as two independent parameters ($a_0$ is the equivalent cubic cell constant of the free standing film and $b$ is the substrate lattice parameter). Such “misfit strain-temperature” diagrams were developed with the aid of thermodynamic calculations for single-domain BaTiO$_3$, PbTiO$_3$, and Pb(Zr$_{1-x}$Ti$_x$)O$_3$ (PZT) films (Pertsev et al. 1998, 2003a). Since the substrate-induced strains lower the symmetry of the paraelectric phase from cubic to tetragonal, the film polarization state may be very different from the ferroelectric phases observed in the corresponding bulk material (see Figure 6.18).

At large negative misfit strains, films of perovskite ferroelectrics stabilize in the tetragonal $c$ phase with the spontaneous polarization $P$ orthogonal to the film–substrate interface, whereas at large positive strains the orthorhombic $aa$ phase forms, where $P$ is directed along the in-plane face diagonal of the prototypic cubic cell. At low temperatures, the stability ranges of the $c$ and $aa$ phases are separated by a “monoclinic gap,” where the monoclinic $r$ phase with three nonzero polarization components $P_i$ becomes the energetically most favorable state. These predictions of the thermodynamic theory were confirmed by the first-principles calculations (Bungaro and Rabe 2004, Diéguez et al. 2004).

It should be emphasized that the orthorhombic and monoclinic phases do not exist in the bulk PbTiO$_3$ crystals, where only the tetragonal ferroelectric state is stable (Haun et al. 1987). In the case of BaTiO$_3$, the $aa$ phase may be compared with the orthorhombic phase forming in the bulk crystal in the low-temperature range between 10°C and −71°C, whereas the $r$ phase can be regarded as a distorted modification of the rhombohedral phase that exists in a free crystal below −71°C (Iona and Shirane 1962).

The most remarkable manifestation of the strain effect appears in thin films of strontium titanate. In a mechanically free state, bulk SrTiO$_3$ crystals remain paraelectric down to zero absolute temperature despite a strong softening of the transverse optic polar mode near $T = 0$ K (Müller and Burkard 1979). The thermodynamic calculations show that this “incipient ferroelectricity” exists in epitaxial SrTiO$_3$ films grown on dissimilar cubic substrates only at small misfit strains ranging from $-2 \times 10^{-3}$ to $-2 \times 10^{-4}$ (Pertsev et al. 2000). Outside this “paraelectric gap,” the ferroelectric phase transition takes place in the SrTiO$_3$ film at a finite temperature, which rises rapidly with the increase of the strain magnitude. The predicted phenomenon of strain-induced ferroelectricity was observed experimentally in SrTiO$_3$ films grown on (110)-oriented DyScO$_3$, which were found to display ferroelectric properties at room temperature (Haeni et al. 2004).

![FIGURE 6.18 Misfit strain-temperature phase diagrams of single-domain BaTiO$_3$ (a) and PbTiO$_3$ (b) thin films epitaxially grown on (001)-oriented cubic substrates. The second- and first-order phase transitions are shown by thin and thick lines, respectively. (From Pertsev, N.A. et al., Phys. Rev. Lett., 80, 1988, 1998. With permission.)](image-url)
The strain-induced increase of the temperature $T_c$ at which the paraelectric to ferroelectric phase transition takes place, is characteristic of all studied perovskite ferroelectrics (Pertsev et al. 1998, 2003a). In addition, the two-dimensional clamping of the film by a thick substrate may change the order of this transition (Pertsev et al. 1998). Strong dependence of $T_c$ on the misfit strain $\nu_m$ explains the very high transition temperatures observed in epitaxial films grown on dissimilar substrates (Choi et al. 2004, He and Wells 2006).

The magnitude of the spontaneous polarization is also sensitive to the lattice strains. This effect is especially pronounced in ferroelectric films grown on "compressive" substrates ($\nu_m < 0$), where the polarization $P$ is orthogonal to the film surfaces. For fully strained BaTiO$_3$ films grown on SrTiO$_3$ ($\nu_m = -2.6\%$), the thermodynamic theory predicts $P_s = 35 \mu C/cm^2$, which is close to the experimental values of 43–44 $\mu C/cm^2$ (Kim et al. 2005, Petraru et al. 2007). Remarkably, the film polarization exceeds the polarization $P_s = 26 \mu C/cm^2$ of bulk BaTiO$_3$ significantly. At the same time, the strain sensitivity of polarization in highly polar Pb-based perovskites, where the ferroelectric ionic displacements are already large in the bulk, is relatively low (Lee et al. 2007).

The enhancement of polarization $P_s$ and the decrease of the in-plane permittivity $\varepsilon_{11}$ in the strained c phase (Koukar et al. 2001) should lead to a considerable increase of the coercive fields $E_c$ in thin films (Pertsiv et al. 2003b). From the Landauer model of domain nucleation (Landauer 1957) it follows that $E_c \sim \gamma^{6/11}/(\varepsilon_{11}^{1/11} P_i^{3/11})$, where $\gamma \sim P_i^2$ is the domain-wall energy. Hence, the coercive field $E_c \sim P_i^{3/11} / \varepsilon_{11}^{1/11}$ of BaTiO$_3$ films grown on SrTiO$_3$ ($\varepsilon_{11} = 170$) may be about eight times larger than that of the bulk crystal ($\varepsilon_{11} = 3600$). Although it is certainly a very strong increase, the strain effect alone cannot explain the observed drastic difference between the measured coercive fields $E_c \sim 150$–300 kV/cm of epitaxial BaTiO$_3$ films (Jo et al. 2006b, Petraru et al. 2007) and the bulk $E_c \sim 1$ kV/cm.

Finally, it should be noted that ferroelectric properties of epitaxial thin films may strongly depend on the orientation of the crystal lattice with respect to the substrate surface. In particular, the phase states and dielectric properties of single-domain PbTiO$_3$ films with the (111)-orientation of the paraelectric phase were found to be very different from those of the (001)-oriented films (Tagantsev et al. 2002).

### 6.5.2 Depolarizing-Field Effect

When the polarization charges $\rho = -\text{div} \, P$ existing at the film surfaces are not perfectly compensated for by other charges, an internal electric field appears in the ferroelectric layer (Figure 6.19). This "depolarizing" field $E_{\text{dep}}$ may be significant even in short-circuited ferroelectric capacitors with perfect interfaces because the electronic screening length in metals is finite (Guro et al. 1970, Mehta et al. 1973).

For a homogeneously polarized film, the electrostatic calculation gives $E_{\text{dep}} = -P_i(\varepsilon_s \varepsilon_0 + c_i)$, where $P_i$ is the equilibrium out-of-plane polarization in the film of thickness $t$, $\varepsilon_0$ is the permittivity of the vacuum, $\varepsilon_s \sim 10$ is the background dielectric constant of a ferroelectric material (Tagantsev and Gerra 2006), and $c_i$ is the total capacitance of the screening space charge in the electrodes per unit area (Ku and Ullman 1964). When $P_i = P_s = 0$ (the c phase), the polarization $P_s(t)$ can be calculated from the nonlinear equation of state $\partial G/\partial P_s = 0$ written for a strained film with an internal field $E_{\text{dep}}$. Since the capacitance $c_i$ affects the polarization only via the product $c_i t$, the dependencies $P_s(t)$ corresponding to different electrode materials can be described by one universal curve $P_s(t_{\text{eff}})$. Here the effective film thickness $t_{\text{eff}}$ may be defined as $t_{\text{eff}} = (c_i/c_i^0) t$, where $c_i^0 = 1/F/m^2$.

Figure 6.20 shows the dependencies $P_s(t_{\text{eff}})$ calculated for fully strained PZT 50/50 and BaTiO$_3$ films grown on SrTiO$_3$ (Pertsiv and Kohlstedt 2007). It can be seen that the spontaneous polarization decreases in thinner films and vanishes at a critical film thickness $t_c$. In the case of capacitors with SrRuO$_3$ electrodes ($c_i = 0.444/4/\mu m^2$), the thickness $t_c$ is about 2 nm for PZT 50/50 films and about 2.6 nm for BaTiO$_3$ films. However, the size-induced phase transition at $t_c$ also predicted by the first-principles calculations (Junquera and Ghozex 2003), cannot be observed in reality since at a slightly larger film thickness $t_c < 3$ nm the single-domain ferroelectric state becomes unstable and transforms into the 180° polydomain state (Pertsiv and Kohlstedt 2007).

The experimental studies of ultrathin BaTiO$_3$ films (Kim et al. 2005, Petraru et al. 2008) showed that the remnant polarization decreases monotonically with decreasing thickness at $t < 30$ nm, where the misfit strain becomes constant. This behavior is similar to the dependence shown in Figure 6.20, but the thermodynamic theory does not provide a precise quantitative description of the experimental data (Kim et al. 2005, Petraru et al. 2008).

The first-principles calculations performed by Junquera and Ghozex (2003) also cannot explain the measured dependence quantitatively (Kim et al. 2005).
For BaTiO$_3$ capacitors with SrRuO$_3$ electrodes, the depolarizing field $E_{\text{dep}}$ has been evaluated experimentally as well and was found to increase dramatically with decreasing film thickness (Kim et al. 2005). Such a strong rise is consistent with the theoretical thickness dependence of $E_{\text{dep}}$ shown in Figure 6.20, which was calculated with the account of the polarization variation $P_{\text{eff}}(t_{\text{dep}})$. The predicted saturation of the depolarizing field and its decrease in ultrathin films, however, were not observed. In this thickness range, the single-domain state becomes unstable (Pertsev and Kohlstedt 2007), and the mean value of the depolarizing field vanishes due to the formation of $180^\circ$ domain structure.

The presence of a depolarizing field in a capacitor is expected to affect the shape of polarization-voltage ($P$-$V$) hysteresis loops and the magnitude of coercive fields (Tagantsev and Gerra 2006, Jo et al. 2006a,b). Indeed, a simple calculation shows that imperfect compensation of polarization charges at the interfaces not only reduces the remanent polarization, but also leads to a tilt of the hysteresis loop (Tagantsev and Gerra 2006). The influence of $E_{\text{dep}}$ on the magnitude of the coercive field seems to be less pronounced. An accurate electrostatic modeling of the polarization switching on the macroscopic level indicates that $E_c$ reduces with decreasing film thickness, but only when the $P$-$V$ loop is not saturated (Tagantsev and Gerra 2006). In the limit of high amplitudes of the driving field applied to a capacitor, the influence of the depolarizing field on $E_c$ disappears. This feature is explained by the absence of voltage drop across the metal–ferroelectric interface at $E = E_{\text{loc}}$, where the macroscopic polarization $P(E)$ goes to zero by definition.

At the same time, Jo et al. (2006a,b) proposed that the depolarizing field may strongly reduce the potential barriers hindering polarization switching in ultrathin films. Such reduction may happen at the early stage of switching, when the macroscopic polarization $P$ is large, but the influence of $E_{\text{dep}}$ becomes negligible in a film with $P = 0$. Therefore, it is not clear whether the coercive field changes. It would decrease if the switching develops as an “avalanche” process after the nucleation of a few reversed domains. On the contrary, the change of $E_c$ should be small when the applied field must increase significantly in the course of switching to facilitate further domain nucleation or domain-wall motion.

It should be noted that the nucleation of reversed domains in a perfect bulk crystal is impossible since the activation energy is many orders of magnitude larger than the thermal energy (Landauer’s paradox). Jo et al. (2006a) suggested that such “homogeneous” domain nucleation becomes possible in ultrathin ferroelectric films, where the field-dependent activation energy decreases dramatically due to strong depolarizing fields. This conclusion, however, is based on a rough estimate of the activation energy obtained in the approximation of a homogeneous depolarizing field, which is valid for a single-domain film only.

Domain nucleation is evidently easier near crystal surfaces, ferroelectric–electrode interfaces, and lattice defects. Gerra et al. (2005) proposed that the interface coupling between a ferroelectric layer and electrodes changes its sign after the polarization reversal and, therefore, stimulates the switching. According to their model, the surface-stimulated nucleation may reduce the coercive field of BaTiO$_3$ down to a value two orders of magnitude smaller than the thermodynamic coercive field. High local electric fields $E_{\text{loc}} > E$ created by spikes on the electrodes may also permit the domain formation at small applied fields $E$. Besides, residual domains probably exist in ferroelectric films, especially in polycrystalline ones. The growth of these domains may play an important role in the polarization switching, as it happens in ferroelectric polymers (Pertsev and Zembilgotov 1991).
6.5.3 Intrinsic Size Effect in Ultrathin Films

Since the unit cells adjacent to the film–electrode interfaces have an atomic environment different from that of the inner cells, the ferroelectric polarization may depend on the film thickness even in the absence of a depolarizing field. This “intrinsic” size effect can be described with the aid of a modified thermodynamic theory based on the concept of extrapolation length (Kretschmer and Binder 1979). In this theory, the total energy of the ferroelectric layer involves an additional surface contribution, and the polarization distribution across the film, in general, is taken to be inhomogeneous.

In the most important case of the (001)-oriented film grown on a compressive substrate ($P_1 = P_2 = 0$, $P_3 \neq 0$), the polarization profile $P_i(x_i)$ can be calculated from the Euler–Lagrange equation (Zembilgotov et al. 2002). For a film having the same atomic terminations at both surfaces and sandwiched between identical electrodes, the boundary conditions can be written as $\partial P_3/\partial x_3 = P_3/\delta$ at $x_3 = 0$ and $\partial P_3/\partial x_3 = -P_3/\delta$ at $x_3 = t$, where $P_3$ is the polarization value at the film boundaries and $\delta$ is the extrapolation length. The polarization suppression (enhancement) near the film surfaces is described by positive (negative) values of the extrapolation length. In a weakly conducting ferroelectric, such as BaTiO$_3$ or PbTiO$_3$, the inner polarization charges $\rho = -\partial P_3/\partial x_3$ are largely compensated by charge carriers so that the associated depolarizing field should be negligible. In this case, the spatial scale of polarization variations is determined by the ferroelectric correlation length $\xi_1^* = \sqrt{\xi_{11}/\rho_3^*}$ of a strained film, and the strength of the intrinsic size effect is governed by the ratio $\xi_1^*/\delta$. (Here $\xi_{11}$ and $\rho_3^*(u_0)$ are the coefficients of the gradient term and the renormalized second-order polarization term in the free energy expansion, respectively.)

The numerical calculations demonstrate that the polarization suppression in the surface layers reduces the temperature $T_c$ of ferroelectric transition at a given misfit strain $u_w$. This reduction, however, is significant only in ultrathin films with thicknesses about a few $\xi_1^*(T = 0)$. Below the transition temperature $T_c(u_w)$, the mean polarization reduces with decreasing film thickness and vanishes at a critical thickness $t_c = \tilde{\xi}_1^*$ (Zembilgotov et al. 2002). Thus, the intrinsic surface effect may lead to a size-induced ferroelectric to paraelectric transformation.

Since the discussed thermodynamic theory is a continuum theory, it is valid only when the characteristic length $\tilde{\xi}_1^*$ of the polarization variations is larger than the interatomic distances. In the case of a negligible depolarizing field, this condition is satisfied at least near the transition temperature $T_c$ because the coefficient $a_3^*$ goes to zero at this temperature (Pertsev et al. 1998). The situation, however, changes dramatically in a perfectly insulating ferroelectric, where the uncompensated polarization charges $\rho = -\text{div} \mathbf{P}$ inside the film create a nonzero depolarizing field (Kretschmer and Binder 1979, Tagantsev et al. 2008). The characteristic length of polarization variations becomes $\xi_3^* = \sqrt{\xi_{11}/(\tilde{a}_3^* + (\varepsilon_3\varepsilon_0)/\delta)}$, which, in contrast to $\xi_1^*$, does not increase significantly near $T_c$. Since $\xi_3^* \sim 0.1\text{nm}$ only, the continuum approach based on the concept of extrapolation length cannot be used to describe the surface effect in perfectly insulating perovskite ferroelectrics (Tagantsev et al. 2008).

In the latter case, however, the ferroelectric film may be assumed to be homogeneously polarized in the thickness direction, and the intrinsic size effect can be described with the aid of a phenomenological approach as well (Tagantsev et al. 2008). To that end, the film free energy is written as the sum of the “bulk” and “surface” contributions, each represented by a polynomial in terms of ferroelectric polarization. In general, the surface contribution should involve not only the even-power terms, but also the odd-power terms, because the surface breaks the inversion symmetry of the ferroelectric (Levanyuk and Sigov 1988, Bratkovsky and Levanyuk 2005). However, when the film–electrode interfaces are identical, the linear term vanishes and the surface energy can be approximated by a quadratic polarization term. The coefficient of this term may be evaluated from the comparison of the phenomenological theory with the results of first-principles calculations performed for ultrathin ferroelectric films. For BaTiO$_3$ capacitors with SrRuO$_3$ electrodes, this procedure reveals that the surface energy is positive (Tagantsev et al. 2008), which implies the polarization suppression at the interfaces.

In other metal/ferroelectric/metal heterostructures, however, polarization could be enhanced near the interfaces. Such enhancement was demonstrated by the first-principles-based calculations performed for ultrathin PbTiO$_3$ and BaTiO$_3$ films (Ghosez and Rabe 2000, Lai et al. 2005). The short-range interactions between the film and electrodes must be also taken into account to prove that this effect exists in ferroelectric capacitors as well. The importance of ionic displacements in the boundary layers of SrRuO$_3$ electrodes for the stabilization of ferroelectricity in ultrathin films was revealed by the first-principles investigations (Sai et al. 2005, Gerra et al. 2006).

6.6 Future Perspective

When the thickness of the ferroelectric layer in a biased capacitor becomes as small as a few nanometers, the quantum mechanical electron tunneling across the insulating barrier should become significant (Kohlstedt et al. 2005b, Zhuravlev et al. 2005a). Since the tunnel current exponentially depends on the barrier thickness, the crossover from a capacitor to a tunnel junction takes place near some threshold thickness. The presence of spontaneous polarization in a ferroelectric barrier and its piezoelectric properties are expected to make the current-voltage ($I-V$) characteristic of a ferroelectric tunnel junction (FTJ) very different from those of conventional tunnel junctions involving nonpolar dielectrics (Kohlstedt et al. 2005b and Rodríguez Contreras 2004). Theoretically, the junction conductance can change strongly after the polarization reversal in the barrier so that the FTJs are promising for the memory storage with nondestructive readout. For the memory applications, asymmetric FTJs with dissimilar electrodes seem to be preferable since such junctions should exhibit...
much larger conductance on/off ratios (Kohlstedt et al. 2005b, Zhuravlev et al. 2005a). This feature is due to the fact that here the mean barrier height changes after the polarization reversal by the amount \[ \Delta \Phi = e P(t) (c_{m1} - c_{m2}) \], where \( c_{m1} \) and \( c_{m2} \) are the capacitances of two electrodes and \( e \) is the electron charge.

The ferroelectric tunnel barrier may also be combined with ferromagnetic electrodes. For such a multiferroic tunnel junction (MFTJ), new functionalities may be expected since the tunneling probability becomes different for the spin-up and spin-down electrons owing to the exchange splitting of electronic bands in ferromagnetic electrodes. In particular, Zhuravlev et al. proposed a new spintronic device, where an electric current is injected from a diluted magnetic semiconductor through the ferroelectric barrier to a normal (nonmagnetic) semiconductor (Zhuravlev et al. 2005b). Their theoretical calculations indicated that the switching of ferroelectric polarization in the barrier may change the spin polarization of the injected current markedly, which provides a two-state electrical control of the device performance.

When both electrodes are ferromagnetic, the tunnel current becomes dependent on the mutual orientation of the electrode magnetizations. This phenomenon, which is termed tunneling magnetoresistance (TMR), is important for the applications in spin-electronic devices such as magnetic sensors and magnetic random-access memories. Since the TMR ratio depends not only on the properties of ferromagnetic electrodes, but also on the barrier characteristics (Slonczewski 1989), it may be sensitive to the orientation of the ferroelectric polarization in the MFTJ. This supposition was confirmed by the theoretical calculations performed for junctions involving two magnetic semiconductor electrodes (Zhuravlev et al. 2005b). It was shown that, under certain conditions, the MFTJ works as a device that allows the switching of TMR between positive and negative values.

The experimental realization of ferroelectric and multiferroic tunnel junctions, however, is a task with many obstacles because it requires the fabrication of ultrathin films retaining pronounced ferroelectric properties at a thickness of only a few unit cells. Moreover, the ferroelectric state with a nonzero net polarization must be stable at such a small thickness and switchable by a moderate external voltage. In our opinion, reliable FTJs showing resistive switching in the tunneling regime have not been fabricated yet, despite several attempts made in this direction (Rodriguez et al. 2003b, Gajek et al. 2007). The observation of a hysteretic \( I-V \) curve or resistance jumps after short-voltage pulses alone is not sufficient to prove the existence of an FTJ (Kohlstedt et al. 2008). Hysteric \( I-V \) curves were also measured for nonferroelectric La\(_{1-x}\)Sr\(_x\)Mn\(_{1-y}\)O\(_3\)/SrTiO\(_3\)/La\(_{1-x}\)Sr\(_x\)Mn\(_{1-y}\)O\(_3\) tunnel junctions and explained by other effects (Sun 2001). Further experiments are necessary to demonstrate the functioning of FTJs unambiguously.

In case the above challenges will be overcome in the future, a number of new exciting opportunities for technological applications and interesting physical phenomena are anticipated. Figure 6.21 summarizes the variety of novel functional oxide tunnel junctions. Here, the Josephson tunnel junctions with a ferroelectric or multiferroic barrier are included as well. The influence of a ferroic tunnel barrier on the Cooper pair and quasiparticle tunneling might lead to interesting new physics. Besides oxide materials, ferroelectric polymers such as PVDF and P(VDF-TrFE) (Xu 1991, Bune et al. 1998) can be incorporated in low-temperature superconducting Josephson junctions [e.g., Nb/Al-AIO\(_x\)-P(VDF-TrFE)/Nb] (Huggins and Gurvitch 1985) and in magnetic tunnel junctions [e.g., Co\(_{53}\)/AIO\(_x\)-P(VDF-TrFE)/Ni\(_{20}\)Fe\(_{80}\)] (Moodera et al. 1995). In principle, one would expect the appearance of physical effects similar to those

![Figure 6.21](image1.png) A “zoo” of novel tunnel junctions involving multifunctional tunnel barriers and electrodes of various types.

![Figure 6.22](image2.png) Low-temperature superconducting Josephson junctions (a) and magnetic tunnel junctions (b) with the AIO\(_x\)-ferroelectric polymer composite barriers.
described above for entirely oxide tunnel junctions. On the other hand, metallic (Josephson and magnetic) tunnel junctions are more reliable than oxide ones, and, in addition, ultrathin PVDF films are compatible with AlO$_x$ so that composite ferroelectric-oxide barriers can be fabricated. The possible structures of superconducting and magnetic metallic tunnel junctions involving PVDF are shown schematically in Figure 6.22.

In conclusion of this section, it should be noted that in addition to the planar metal/ferroelectric/metal multilayers discussed above, heterostructures of other geometries may be useful for certain applications in nanoelectronics and may even display specific physical properties. Remarkably, one-dimensional structures in the form of ferroelectric nanowires (Urban et al. 2003) and nanotubes with inner and outer electrodes (Alexe et al. 2006) have been successfully fabricated. Ferroelectric quantum dots are of great interest as well, in particular, for electro-optical devices (Ye et al. 2000).

### 6.7 Summary and Outlook

The overview presented in this chapter demonstrates impressive achievements in the deposition, characterization, and theoretical description of nanoscale ferroelectric films and heterostructures. Remarkably, capacitors involving only a few nanometers of perovskite ferroelectrics were successfully fabricated, displaying a high remanent polarization. Several advanced analytical tools are now available, showing that high structural quality and sharp interfaces can be retained even in nanoscale capacitors. The basic physical effects in ferroelectric thin films, such as the strain and depolarizing-field effects, are already well understood theoretically, and the influence of short-range interactions at the ferroelectric–metal interfaces is intensively studied by first-principles calculations. Thus, all three constituents of the research triangle shown in Figure 6.1 are functioning effectively, which promises new advances in the physics of nanoscale ferroelectrics and their device applications in the near future.

### References


