Epitaxial integration of perovskite-based multifunctional oxides on silicon

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Abstract

We review recent developments in the epitaxial integration of multifunctional oxide thin film heterostructures on silicon (Si). Perovskite oxides have been extensively studied for use in multifunctional devices due to a wide range of functional properties. To realize multifunctional oxide devices, these multifunctional films should be integrated directly on Si, maintaining high crystalline quality. Molecular beam epitaxy growth of epitaxial SrTiO₃ (STO) on Si provides a template for incorporating the epitaxial oxide films on Si. However, the dissimilar physical nature of Si from most oxide materials influences the properties of oxide films on Si, especially with regard to structural defects and thermal strains. Therefore, in this review, we present a comprehensive overview of epitaxial integration of various model oxide systems on Si, addressing how STO/Si can be used to explore the novel phenomenon of oxide heterostructures as well as to realize multifunctional devices.

Keywords: Thin Films; Oxides; Epitaxy

1. Introduction

Epitaxial heterostructures of perovskite-type oxides have attracted much attention due to their enormous range of electrical, magnetic and optical properties. For example, metallic conductors, dielectrics, ferroelectrics, piezoelectrics, semiconductors, ferromagnetics, superconductors, non-linear optics and multiferroics have been demonstrated in perovskite oxides. The combination of cations within perovskite unit cells and the mixture of two or more different perovskite materials give rise to many unusual, but scientifically and technologically interesting, phenomena, such as colossal magnetoresistance and giant piezoelectricity. Beyond the bulk effects of oxides, the recent discovery of two-dimensional electron gas (2DEG) at the LaAlO₃ (LAO)/SrTiO₃ (STO) interface have led researchers to explore the novel physics arising at oxide heterointerfaces.

It would be reasonable to take the approach of integrating the functionality of oxides into a Si-based platform to realize multifunctional devices. In this sense, it is highly desirable to develop methods to compatibly combine these two different materials with high stability. However, Si has high reactivity with oxygen and many other elements, and this presents a formidable challenge to the direct integration of functional oxides with silicon (Si). Therefore, various buffer layers on Si have been studied to fabricate a virtual substrate to grow epitaxial perovskite oxides [1–7].

The exquisite control offered by the molecular beam epitaxy (MBE) technique has enabled the direct integration of epitaxial STO thin films on Si. McKee et al. [8] reported the epitaxial growth of STO films on (001) Si by MBE, motivated by the search for new gate dielectrics replacing SiO₂. Since then, many researchers have succeeded in growing epitaxial STO on Si [9–14] and demonstrated that it can be used as a template to grow perovskite-type multifunctional oxides on Si. STO has been commonly used as a single-crystal substrate for epitaxial growth of multifunctional oxides. STO has a lattice parameter of 3.905 Å with a simple cubic structure (space group, Pm3m) close to most other perovskite oxides. Furthermore, the technique is well
developed for the control of surface termination with atomical smoothness, which is critical for investigating interfacial effects. Therefore, epitaxial growth of STO on Si allows for the investigation of oxides with Si-based devices while maintaining their functionalities.

Epitaxial STO thin films on Si substrates affect the properties of the oxide heterostructures on top of them. First, with the growth conditions and STO thickness, the as-grown strain state of epitaxial STO on Si varies from compressive to tensile. Second, thermal strain, which is generated by the thermal expansion coefficient of Si which is smaller than that of oxides, induces an additional biaxial tensile strain to the epitaxial strain during cool-down from growth temperature. Third, Si (or the thin SiO2 layer between STO and Si) imposes different mechanical boundary conditions than oxides do, which critically affects the piezoelectric response in electromechanical devices. Fourth, the large lattice mismatch between STO and Si generates defects that may affect the physical properties of the heterostructures, including the antiphase boundary, dislocation and in-plane mosaic structure. Besides these, the formation of a SiO2 amorphous layer between STO and Si and the evolution of new electrical orders (ferroelectric, polar or relaxor behavior) in the strained STO layer may be important factors to consider in order to successfully integrate multifunctional oxides in Si. The effects of these unique conditions in STO/Si may vary from material to material. We will review how these issues are involved in the property changes of oxide thin films through specific model systems.

2. Quasi-single-crystal SrTiO3 on Si

Fig. 1 shows a cross-sectional transmission electron microscopy (TEM) image of the epitaxial STO/Si interface. A clear interface between the single-crystal STO film and Si substrate was observed without the SiO2 layer. The lattice parameter of Si was 5.4307 Å, while that of STO was 3.905 Å. Due to the large lattice mismatch between them, the epitaxial STO had to be grown 45° rotated with respect to the Si unit cell, which has a better lattice match between the lattice parameter of STO and half of the diagonal distance of the Si unit cell (3.840 Å).

One of the major questions regarding epitaxial STO/Si is about its quality: is it better or worse than bulk STO single crystals, and if it is worse, can we improve it by post-treatment? The quality of STO/Si as a substrate mainly concerns the crystalline quality, chemical stability and the well-defined, atomically smooth surface. Although the quality of STO/Si was determined first by the growth technique, it can be further improved with post-treatment by thermal annealing and buffered hydrofluoric acid (BHF) etching [15]. As-grown STO films on Si have many defects. This makes it difficult to etch the as-grown STO surface to achieve a single TiO2 termination because the STO surface becomes severely damaged by BHF etching, causing the high density of large and deep etch pits to remain. Thus, in order to improve chemical stability and crystalline quality, thermal annealing was followed by BHF etching.

Fig. 2a shows the out-of-plane (002) STO rocking curves of as-grown and annealed (100 nm) STO templates on (001) Si substrates. After annealing at 900 °C for 2 h in an oxygen atmosphere, the full width at half maximum (FWHM) improved from 0.008° to 0.006°, showing an improvement in the crystalline quality of the film. It is also important to note that the FWHM of the STO film was much narrower than that of the STO bulk single crystals (0.035–0.108°). However, off-axis azimuthal scans of STO templates exhibited significantly broader in-plane mosaic spread compared with bulk single crystals (0.022°), although the FWHM of the 101 scan improved from 0.78° to 0.64° after annealing (Fig. 2b). This is attributed to the large lattice mismatch of 1.7% between STO (3.905 Å) and Si (3.840 Å; half of the diagonal distance). It was also found that the in-plane lattice parameter of the annealed STO template was 3.914 Å, indicating that it is under in-plane tensile stress due to the thermal strain arising from the thermal expansion mismatch between STO (~9 × 10^{-6} K^{-1}) and Si (~2.5 × 10^{-6} K^{-1}).

The BHF-etched STO template followed by annealing exhibited an atomically smooth surface with single-unit-cell steps (Fig. 2c−e). Note that these steps are non-periodic due to the exact Si substrate (miscut angle, χ < 0.05°). A periodic step-terrace structure similar to STO single crystals was observed in the STO template on the miscut Si substrate. A significant reduction of dislocation density in oxide films by post-annealing was reported [16,17]. Therefore, it is possible that the chemically stable surface of the annealed STO template can be attributed to the reduction in the density of defects, such as dislocations, as well as the reduction of low-angle grain boundaries through grain growth. Thus, we believe that BHF treatment allows for the creation of a TiO2-terminated surface of an annealed STO template. In particular, the atomically smooth TiO2-terminated surface of the STO template leads to the possibility of creating functional oxide heterointerfaces, such as 2DEG on a Si platform, which will be discussed later.

The post-annealing significantly enhances the quality of the epitaxial thin films grown on STO/Si. 50 nm thick epitaxial SrRuO3 metallic oxide thin films [18,19] were grown on the top of the as-grown and annealed STO/Si templates by 90° off-axis sputtering [20,21] in order to study the influence of the surface and crystalline quality of STO templates on the growth of the epitaxial thin films of multifunctional oxides. SrRuO3 (SRO) is a conductive perovskite oxide that is commonly used as a bottom electrode in the epitaxial heterostructures [22]. Fig. 3a and b shows the out-of-plane (220) SRO rocking curves and the in-plane (112) SRO phi scans of the epitaxial (110) SRO films on the as-grown and annealed STO/Si templates, respectively. The FWHM rocking curve of the SRO film on the as-grown STO/Si template was 0.15°, whereas the SRO film on the annealed STO/Si template exhibited a very narrow FWHM of 0.04°, which is the lowest value for epitaxial...
Fig. 1. (a) Schematic illustration of the epitaxial oxide heterostructure on Si and a cross-sectional TEM image of STO/Si interface. (b) Schematic illustration of the epitaxial relationship between perovskite oxides and Si unit cells.

Fig. 2. (a) Out-of-plane (002) STO rocking curves and (b) in-plane (101) STO phi scans of 100 nm thick STO templates on Si substrates before and after annealing at 900 °C for 2 h. AFM image of surface morphology of (c) as-grown, (d) annealed and (e) BHF-etched STO/Si. Figures are adapted from Ref. [15].

SRO films on Si ever reported. The FWHM phi scan of the SRO film on the annealed STO/Si template was also lower than that on the as-grown STO/Si template, as shown in Fig. 3b. The phi scan FWHMs of SRO films on the as-grown and annealed STO/Si templates were 0.80° and 0.65°, respectively. Fig. 3c and d shows the atomic force microscopy (AFM) images of SRO films on the as-grown and annealed STO/Si templates, respectively. The SRO film on the as-grown STO/Si template exhibited an irregular surface morphology, which varied in step height from 4 to 12 Å. In contrast, the SRO film on the annealed STO/Si template exhibited a much smoother surface and more regular steps. In addition, approximately single-unit-cell high steps were observed on the surface of the SRO film on the annealed STO/Si. These results indicate that the crystalline quality and surface morphology of epitaxial SRO films strongly depend on the quality of STO templates.

3. Multiferroics on Si

Epitaxial thin films of BiFeO₃ (BFO) have been extensively investigated for magnetoelectric devices as well as lead-free ferroelectric/piezoelectric devices. BFO is multiferroic at room temperature; ferroelectric, ferroelastic and antiferromagnetic orders coexist in a single phase [23–26]. The spontaneous polarization along the [111] direction in the rhombohedral unit cell was coupled with (1 1 1) antiferromagnetic planes. Both electric and magnetic orders were coupled through the ferroelasticity of the rhombohedral unit cell, enabling electrical control of the magnetic property [27–30]. Another interesting feature is the giant ferroelectric property of BFO: BFO has the largest remanent polarization ($P_r \approx 100 \mu C \cdot cm^{-2}$) along the [111] polar axis among any known ferroelectrics. This makes BFO a promising candidate for high-density ferroelectric memory devices.

Due to the rhombohedral symmetry of BFO with $a_{pc} = 3.964 \AA$ and $\alpha = 89.4^\circ$ (“pc” stands for pseudo-cubic), BFO can form complex domain structures. A thin film grown on a (001) SrTiO₃ substrate can exhibit a maximum of four structural (ferroelastic) variants and eight ferroelectric variants [31,32]. Complex domain structures can form three different domain walls: $71^\circ$, $109^\circ$ and $180^\circ$. Each domain wall has a different crystallographic plane and electrical configuration, resulting in different electrical, magnetic and elastic properties [33–38]. Therefore, the domain and domain wall structure directly affect the physical properties of BFO films.

In this section, we will review how miscut Si can enhance the ferroelectric properties of BFO films by domain engineering. Further, we will see how BFO heterostructures on Si substrates can be used to explore the strain effect.

![Fig. 3. (a) Out-of-plane (220) SRO rocking curves and (b) in-plane (112) SRO phi scans of 50 nm thick epitaxial SRO films grown on as-grown and annealed STO/Si templates by sputtering. AFM images of 50 nm thick epitaxial SRO films grown on (c) as-grown and (d) annealed STO/Si templates by sputtering. Scan size is $5 \times 5 \mu m^2$. Figures are adapted from Ref. [15].](image)
on ferroelectricity and improve the electrical property fabricating free-standing BFO membranes, which cannot be done with BFO films on bulk single-crystal substrates.

3.1. Enhancement of ferroelectric property by domain engineering by miscut Si

The use of a miscut substrate is a very simple but powerful tool for engineering the domain structure of low-symmetry thin films [33,39–42]. The miscut angle and in-plane direction cause symmetry breaking on the surface of substrates, resulting in a preferential formation of particular domains. It was demonstrated that monodomain BFO thin films were grown on SRO/STO substrates with 4° miscut along [110]. The bottom electrode stabilized the ferroelectric monodomain by effectively screening the depolarization field [43–45]. BFO films with a reduced number of variants exhibited superior ferroelectric properties. Wang et al. [46] reported the growth and properties of epitaxial BFO on STO/Si substrates with a relatively small value of remanent polarization (\(\sim 45 \mu C \cdot cm^{-2}\)) compared to films on (001) STO substrates. Enhancement of ferroelectric properties was achieved by domain engineering using STO on Si with a 4° miscut along [110], which had two ferroelectric domains. BFO films were grown using the off-axis radio-frequency sputtering technique [47].

Fig. 4a shows the X-ray diffraction (XRD) \(\theta–2\theta\) scans of 200 nm BFO films on (001) Si with an exact and 4° miscut toward [110]. Prior to growing BFO, a 100 nm SRO film was deposited for the bottom electrode. The epitaxial BFO thin films grew without any secondary phase or random orientations, which is the first step in integrating epitaxial BFO into a Si platform. Similar high quality epitaxial films with a thickness of 600 nm were also grown to compare the crystalline quality and size effect of BFO on Si. The out-of-plane lattice parameters of 200 nm BFO films were calculated to be 3.962 Å and 3.955 Å on exact and 4° miscut Si substrates, respectively. However, for 600 nm BFO, the out-of-plane lattice parameters were nearly the same (3.945 Å) for the films on the exact and 4° miscut Si substrates. Note that the thicker BFO films had a smaller c-lattice parameter. BFO films grew with biaxially compressive strain at growth temperature (690 °C) due to the lattice mismatch. Thicker (600 nm) BFO films had smaller compressive strain than thinner (200 nm) ones at growth temperature due to the strain relaxation. When they were cooled to room temperature, tensile strain driven by thermal mismatch compensated for the compressive strain. The dominant thermal strain caused both samples to be under tensile strain at room temperature.

Fig. 4b shows the FWHM of the (002) pc BFO. It is clearly visible that the films grown on exact Si substrates had a wider rocking curve width, irrespective of the thickness of the films. The FWHM of the rocking curve for the (002)pc BFO reflection for 200–600 nm thick films ranged from 0.8 to 1.3 on exact Si and from 0.25 to 0.42 on the 4° miscut Si substrates. The narrow rocking curve width of BFO on the miscut Si represented the high crystalline quality of the BFO films on high miscut substrates. This high crystal quality may have come from two sources: (1) the stoichiometric composition of BFO suppressing the volatile species, Bi₂O₃, by a high density of steps; or (2) the simple domain structure with the reduced number of variants. It was confirmed by PFM and TEM that the BFO film on the 4° miscut Si had two variants, while that on the exact Si had four variants. Cross-sectional TEM (Fig. 4c and d) revealed that the two-variant BFO film had only well-aligned 71° domain walls with periodic spacing, while the four-variant BFO film had both 71° and 109° domain walls with entangled and complex configuration.

![Fig. 4. (a) X-ray diffraction \(\theta–2\theta\) scans for the 600 nm BFO thin films on 0° and 4° miscut (001) Si. Cross-sectional TEM images of BFO grown on (c) 0° and (d) 4° miscut Si.](http://dx.doi.org/10.1016/j.actamat.2012.09.073)
The ferroelectric properties of BFO films were measured by polarization vs. the electric field hysteresis loop (P–E loop) measurement, as shown in Fig. 5. The remanent polarization (Pr) of the four-variant (600 nm) BFO film was 42 ± 3 μC cm⁻², which is consistent with the report from Wang et al. The P–E loop was not well saturated, with both ends opened with increasing Pr with the applied electric field. This indicates that the leakage current through the BFO film significantly affected polarization switching. Moreover, the P–E loop was not vertical, but slanted. On the other hand, the two-variant BFO film showed a well-saturated, vertical P–E loop with an enhanced Pr of 57 ± 3 μC cm⁻², which is the highest Pr ever reported for the (001)-oriented epitaxial BFO film on Si. This enhancement of the ferroelectric property of the domain-engineered two-variant BFO films is attributed to the absence of the 109°/C176 and 180°/C176 domain walls, which are more conductive than the 71° domain wall. Furthermore, the well-aligned domain wall structure of the two-variant BFO film reduced the possible domain wall pinning sites, which was observed in the samples with complex, entangled domain wall structures. Note that the Pr of BFO film on Si was still lower than that on STO, although both had the same domain structure of the two variants. This is due to the strain effect on polarization: the biaxial tensile strain imposed on BFO on Si reduced the projection of the switched polarization along the out-of-plane direction. This will be discussed in detail later.

3.2. Free-standing BFO membrane

Emerging flexible device technology, such as displays, smart cards and embedded sensors, requires the integration of functionality on the various flexible platforms. Most flexible substrates are organic materials, limiting the high temperature process of oxide syntheses. One method is to transfer the functional layers grown on the conventional, rigid substrate at a high temperature into the desired flexible substrates. An Si substrate can be a sacrificial substrate, used to transfer oxide films grown on it to other platforms by selectively etching only Si [48,49]. The fabrication process of epitaxial (001) BFO membranes separated from the Si substrate is described with schematic diagrams in Fig. 6. The Si substrate was dry-etched from the back side by inductively coupled plasma, and the SRO bottom layer acted as an etch-stop layer due to its chemical stability. This method will work for most epitaxial oxide heterostructures on Si.

Fig. 7a shows the XRD θ–2θ scans of a 400 nm as-grown BFO film on (001) Si and a BFO membrane separated from Si. For the BFO membrane, the (004) Si peak disappeared and the diffraction peaks from the Au counter electrode deposited during the lift-off process were observed. The shift of 00l peaks toward lower diffraction angles after membrane fabrication indicates a relaxation of strain with an expansion of the out-of-plane lattice parameter of the film. The out-of-plane lattice parameter of the as-grown film was found to be 3.943 Å, which is smaller than that of bulk BFO, 3.964 Å, due to the thermal strain. As can be seen in the inset of Fig. 7a, when released from the Si substrate, the out-of-plane lattice parameter of BFO film became that of bulk BFO, suggesting that the elastic strain of the as-grown film is fully relieved.

The two-variant domain structure of BFO films on Si was maintained even after release from Si in the BFO membrane, which was confirmed by high resolution XRD (HRXRD) reciprocal space maps (RSMs). Fig. 7b shows the RSMs of the as-grown 400 nm BFO film around the (113)pc peak. The obtained RSMs showed two peaks as a consequence of the existence of two domains. The RSMs for the BFO membrane in Fig. 7c also showed peak splitting into two domains, indicating that the overall domain structure was maintained after the lift-off process. The diagonal peak shape seen for the membrane indicated that the strain relief led to an increase of the mosaic spread of the film along the (101)pc domain walls. The as-grown film was found to possess two different d-spacings for the (113)pc reflection, but the membrane contained three different d-spacings. Therefore, the HRXRD RSM results confirm that the crystal structure of the BFO membrane is rhombohedral, while that of the as-grown film is monoclinically distorted.

Fig. 6. Schematic diagrams showing the fabrication process of strain-free BFO membranes: (1) epitaxial growth of BFO/SRO/STO/Si heterostructures; (2) deposition of Pt top electrodes; (3) bonding the capacitor structure onto a supporting wafer; (4) removal of the Si substrate by inductive plasma etching; (5) Au electroplating; (6) final structure after detachment of the membrane from the supporting wafer by dissolving the adhesive in acetone. Figures are adapted from Ref. [48].

Fig. 7. (a) HRXRD $\theta$–$2\theta$ scans of 400 nm BFO films before and after lift-off. ■ and ● Correspond to the diffraction peaks from Pt top electrodes and the Au plate, respectively. The insets show an expanded view around the (002)$_{pc}$ peaks, with the vertical line for the $2\theta$ value of bulk (002)$_{pc}$ BFO. Reciprocal-space maps around the (113)$_{pc}$ peak of the 400 nm as-grown film on (a) Si and (b) membrane. Figures are adapted from Ref. [49].
The BFO membrane offers an excellent opportunity to explore the coupling effect between lattice strain and polarization. By measuring the \( P–E \) loop of BFO film before and after release of Si substrate, as shown in Fig. 8a, we could correlate the change of strain state with that of \( P_r \). Two different \( P_r \) values measured from the 400 nm and 600 nm BFO films on Si showed exactly the same value after strain release. The result is consistent with that in the compressive strain regime, where the strain states of films were controlled by varying thicknesses of films on the STO substrate (Fig. 8b). It should be noted that the variations of sample-to-sample and capacitor-to-capacitor were ruled out in this data by measuring exactly the same capacitor before and after strain release. This study about the strain effect on BFO ferroelectricity reveals that (001) pc BFO has a strong coupling between the strain and ferroelectricity: (001) pc BFO films exhibited a \( \sim 25\% \) change in \( P_r \) for a 1.0% in-plane strain. This is higher than the 16% change in \( P_r \) for PbTiO\(_3\) [50,51] and is comparable to the 33% change in \( P_r \) for BaTiO\(_3\) [52] for the same amount of in-plane strain. This result is in contrast with the very small strain dependence of \( P_r \) (1 1 1) BFO films (\( \sim 1.3\% \) change in \( P_r \) for a 1.0% in-plane strain) that was predicted by the theoretical simulation [53]. From the measurements of the \( P–E \) hysteresis loops of the BFO films on the STO and Si substrates from room temperature to 8 K, we found that there was no temperature dependence of \( P_r \) values for (001) pc BFO films, which indicates that the strong strain dependence of \( P_r \), in (001) pc BFO is valid over a wide range of temperatures. These experimental results suggest a model of strain-induced polarization rotation to explain such strong strain-dependence of polarization [49].

Relieving the substrate clamping effect from the BFO film improved the electrical properties, such as leakage current and dielectric breakdown, in free-standing BFO membranes. It is widely accepted that oxygen vacancies formed during growth cause a portion of the Fe\(^{3+}\) ions to become Fe\(^{2+}\), which is responsible for the high leakage current in BiFeO\(_3\) [54]. Based on this, we suggest that the breakdown during the fatigue test could be due to the formation of conducting filaments as they gather mobile defects, such as oxygen vacancies. Fig. 9a shows that the membrane has a lower leakage current than the as-grown film. Although further study is needed to identify the exact mechanism of the reduction in the leakage current in the free-standing BFO membrane, such reduction helps prevent breakdown during fatigue cycles.

Fatigue is one of the most important factors in determining the reliability of ferroelectric and magnetoelectric devices. Fig. 9b shows the fatigue characteristics of a 400 nm (001) pc as-grown film and membrane. The amplitudes of the switched polarization for the as-grown films and membranes were very close to the \( 2P_r \) values, indicating that the switching field of \( \pm 160 \text{ kV cm}^{-1} \) provides complete switching in both cases. The capacitors with the Pt top electrode in both BFO films on the Si and free-standing BFO membrane remained fatigue-free to \( \sim 1 \times 10^9 \). Such fatigue resistance behavior is attributed to the simple 71° switching path during fatigue cycles, which suppresses the formation of domain pinning sites. However, the breakdown property is quite different: the capacitors of the BFO film on Si showed breakdown at \( \sim 1 \times 10^9 \) cycles, while the BFO membrane remains survived without breakdown to \( 2.4 \times 10^{10} \) cycles. For the 600 nm BFO membranes, we observed a very similar result, confirming the fatigue-free behavior with a breakdown-proof characteristic in the BFO membranes. The reduction in the leakage current and easy domain wall motion during 71° switching that arose from freeing the BiFeO\(_3\) film from substrate clamping prevented breakdown during the fatigue test and thus led to the observed fatigue-free behavior.

4. Giant piezoelectrics on Si

Smart materials that can sense, manipulate and position are crucial to the functionality of micro- and nano-machines. The integration of single-crystal piezoelectric films on Si offers the fabrication of high performance piezoelectric...
microelectromechanical systems (MEMS), incorporating all the advantages of large scale integration of Si substrates with on-board electronic circuits in a manner that may radically improve performance at a significantly lower cost [55–62]. Lead-based relaxor-ferroelectric single crystals, such as Pb(Mg1/3Nb2/3)O3 [55–62]. Lead-based relaxor-ferroelectric single crystals, such as Pb(Mg1/3Nb2/3)O3 (PMN–PT), are known to have extremely large piezoelectric response compared to the conventional Pb(Zr,Ti)O3 material, and are utilized in bulk actuation and sensor devices [63,64]. It is highly desirable to achieve such high piezoelectric thin films integrated with Si.

PMN–PT exhibits giant piezoelectric properties only when particular conditions are satisfied [63]: (1) single-crystal forms with (001)pc orientation, (2) pure perovskite phase without the pyrochlore phase and (3) stoichiometric composition near the morphotropic phase boundary. For this to be accomplished, it is necessary to deposit high-quality films with excellent control. However, this has long been hampered by the extreme difficulties of synthesizing the phase-pure, high crystalline and stoichiometric PMN–PT films. For example, the 3.5 μm PMN–PT film on the exact Si exhibited a large volume of pyrochlore phase and polycrystalline perovskite phase, as shown in Fig. 10a. The difficulty in making phase-pure perovskite PMN–PT films arises mostly from compositional variations in films that are extremely sensitive to the deposition conditions due to the volatile PbO species, easily resulting in non-stoichiometric films. In order to suppress the formation of the lead-deficient pyrochlore phase, STO/Si with a 4° miscut toward [1 1 0] was used to deposit PMN–PT using the sputtering technique [65]. The 3.5 μm PMN–PT film on 4° miscut Si showed a dramatic improvement in terms of both phase purity and epitaxy of the perovskite phase. It had no detectable pyrochlore phase, as shown in Fig. 10b. This is attributed to the fact that the high density of steps on the surface of the miscut substrates effectively incorporated the volatile constituents into the film, leading to the stoichiometric films. Azimuthal φ scans of this phase-pure PMN–PT film (Fig. 10c) showed in-plane epitaxy with a cube-on-cube epitaxial relationship, [100]pc PMN–PT/[100]pc SrRuO3/[110]SrTiO3/[110] Si. TEM analysis also confirmed epitaxial growth of the PMN–PT heterostructure on Si. The high-resolution TEM image (Fig. 10d) exhibited an atomically sharp interface between the SRO and PMN–PT layers; the epitaxial match between the layers was clear. It was observed that the high density of the anti-phase boundaries of the STO propagates to the PMN–PT layers. This is due to the large out-of-plane lattice mismatch between Si and oxide layers at the vicinal steps of the Si substrate. Although further study is needed to identify the defect–property relationship, the anti-phase boundary and dislocation do not seem to critically affect the piezoelectric performances of PMN–PT films with a range of 300 nm to 1 μm thickness as they exhibit similar a piezoelectric response as a bulk single-crystal PMN–PT, as will be discussed later.

Fig. 11a shows the P–E loop of the 1 μm PMN–PT thin films on STO and STO/Si. The positive P, values of PMN–PT films were ~33 μC cm−2 with a square-like shape of the P–E loop on the STO substrate, and ~19 μC cm−2 with a slanted P–E loop on STO/Si. This is due to the different strain states of the PMN–PT films on STO and STO/Si. XRD data revealed that PMN–PT on STO/Si had a smaller out-of-plane lattice parameter (4.022 Å) than that on STO/Si (4.061 Å) due to the thermal strain. This strain vs. the P–E loop relationship is consistent with that of the BFO films, as shown in Fig. 8a. Although the P, value of PMN–PT on STO/Si was reduced by the slanted shape of the P–E loop, the strong imprint by built-in bias increased positive P, up to ~19 μC cm−2. This increase of P, led to the enhancement of piezoelectric response. The imprint also stabilized a certain direction (downward) of polarization, resulting in significantly less aging in the piezoelectric response [66] and more robustness against depolarization due to voltage or temperature excursions [67]. This imprint was also reflected in the shift of relative
dielectric permittivity data, as seen in Fig. 11b. This lowered the dielectric permittivity at the zero electric field, which is favorable for energy harvesting figure of merit, as will be discussed later. Such a strong imprint, not seen in bulk PMN–PT single crystals [68], may be due to the asymmetric nature of top and bottom interfaces between the electrodes and the PMN–PT layer.

The $\varepsilon_{31,f}$, the transverse piezoelectric coefficient, was the material’s figure of merit for the majority of the micromachined piezoelectric sensors and actuators. The PMN–PT films on Si showed the highest $\varepsilon_{31,f}$ value of 27 C m$^{-2}$/V, measured by wafer flexure, which are the highest reported among any other piezoelectric thin films. Moreover, the figure of merit for MEMS piezoelectric energy harvesting, $\varepsilon_{31}/\varepsilon_{33}$ (relative dielectric permittivity) [69,70], showed a higher value than PZT films. Such a high value originated from the high $\varepsilon_{31,f}$ value and lower $\varepsilon_{33}$ due to the imprint (Fig. 11b). This indicates that the performance of the voltage-driven sensors will be enhanced over conventional PZT materials. Fig. 11c compares PMN–PT film’s figure of merit with PZT and other piezoelectric materials, demonstrating the advantages of these PMN–PT films for piezoelectric and energy-harvesting devices.

One of the advantages to using a Si substrate is the possibility of using a conventional microfabrication process that is well developed in the Si industries. Fig. 12 describes a microfabrication process for making PMN–PT cantilevers, which is the prototypical device structure using transverse piezoelectric response (31 mode). A blanket PMN–PT heterostructure (Fig. 12a) was fabricated with the following thicknesses for each layer of the stack: Pt (60 nm)/PMN–PT (270 nm)/SrRuO$_3$ (100 nm)/SrTiO$_3$ (13 nm)/(001) Si substrate. The Pt and PMN–PT layers were then ion-milled to expose the SrRuO$_3$ using S1813 photoresist as a mask. Ar$^+$ ion-milling was conducted at etch rates of ~50 nm min$^{-1}$ for Pt, ~30 nm min$^{-1}$ for PMN–PT and ~15 nm min$^{-1}$ for SrRuO$_3$. The sample was cooled to ~190 K during etching to prevent burning of the photoresist. Pt bottom electrode contact pads were patterned using a lift-off process, as shown in Fig. 12b. To define the active regions (cantilevers or beams),

![Fig. 10. X-ray diffraction pattern measured using a 2-D area detector of the PMN–PT heterostructure on the (001) Si substrates with (a) 0° miscut (±0.1°) and (b) 4° miscut along [110]. The pyrochlore phase was identified as Pb$_2$Nb$_2$O$_7$. Pseudo-cubic notations are used for both PMN–PT and SRO peak indexing. (c) Phi-scan of the (101)$_{pc}$ PMN–PT and (202) Si diffraction peaks. (d) High-resolution TEM image of PMN–PT and SRO interface. Figures are adapted from Ref. [65].](image)
ion-milling was performed with a thicker photoresist (S1827) as a mask until the Si substrate was exposed, as shown in Fig. 12c. An inductively coupled plasma (ICP) etch with 0.93 Pa (7 mTorr) $\text{SF}_6: \text{O}_2 = 1:1$ was used to etch Si for 30 min. The plasma etched Si from the exposed Si side walls, releasing the PMN–PT cantilevers (Fig. 12d). Note that this plasma etching did not attack the other layers significantly during Si undercut. Note that all the as-fabricated cantilevers were bent downward after release from the Si substrate (Fig. 13a, inset). The tensile strain, originally dominant by Si thermal mismatch, then vanished after etching Si, and epitaxial strain between PMN–PT ($a_{pc} = 0.402 \text{ nm}$) and SRO ($a_{pc} = 0.393 \text{ nm}$) became dominant. Then, due to the larger thickness and lattice parameter of the PMN–PT layer over SRO, strain relaxation occurred to bend the cantilever downward.

Fig. 13a shows the measured profile of a 34 $\mu$m long cantilever as a function of applied voltage. Due to the downward-poled state in the as-grown PMN–PT films by a strong imprint, no additional poling process was necessary. When positive voltage was applied to the top electrodes, the PMN–PT film was contracted laterally through the transverse piezoelectric response. This caused upward bending of the cantilevers with the neutral plane off-centered by the structural asymmetry between the top (60 nm Pt) and bottom ($\sim 110$ nm SRO/STO) layers. The tip moved $0.375 \pm 0.005 \mu\text{m}$, as shown in Fig. 13b. Finite element simulation was performed using the material parameters reported for bulk single crystal 0.67 PMN–0.33 PT. The experimental and modeled results are consistent, as shown by the solid and dotted lines in Fig. 13b, respectively. This indicates that the superior piezoelectric properties of PMN–PT films survive in the device structure after going through the microfabrication process. It is remarkable that the PMN–PT cantilevers can significantly lower the driving voltage to achieve the same displacement as the electrostatic cantilevers with comparable geometry (simulation result), as shown in Fig. 13b.

The actual displacement of the cantilever also depends on geometry; for example, the thickness of the passive layer beneath the piezoelectric layer [71]. Si on insulator substrates will enable more complex device structures with precisely controlled passive layer thicknesses to control stiffness and displacement. They will provide a wide range of piezoelectric device applications, such as ultrasound medical imaging, micro-fluidic control, piezoelectronics and energy harvesting. Beyond electromechanical devices, epitaxial heterostructures with giant piezoelectricity will provide a new method for adjusting and modulating multifunctional properties, such as ferroelectric, ferromagnetic, superconducting and multiferroic materials, by dynamic strain control [72,73].

5. Two-dimensional electron gas on Si

Interfacial effects have attracted much attention in the exploration of new physics emerging from the novel configuration of structural, chemical and physical states [74]. Progress in the thin film deposition process has enabled an atomic level of controlled growth of multiple materials with atomically sharp interfaces, which is a prerequisite for identifying the interplay between charge, spin, orbital and lattice at the symmetry-broken interface. One of the remarkable new discoveries with regard to the oxide interface is 2DEG formation at the two band insulators, STO.
and LaAlO$_3$ (LAO) [75–87]. This has launched many experimental and theoretical investigations of the fundamental origins and properties of this novel electronic state. Electrical control of a metal–insulator quantum phase transition was demonstrated at room temperature [80]. At low temperatures, another electric-field-induced quantum phase transition, from insulating to superconducting, was observed [81]. Moreover, the coexistence of ferromagnetism and superconductivity, which is rare in nature due to their mutually exclusive characteristics, has attracted a great scientific interest [88, 89]. Cen et al. [75] demonstrated nanoscale lateral confinement of 2DEG using a conducting atomic force microscope (c-AFM) lithography technique. Metallic nanoislands, nanowires and transistors were constructed with characteristic dimensions approaching one nanometer, without the need for complex lithographic techniques.

**Fig. 12.** (a) Epitaxial PMN–PT heterostructure on Si substrate. (b) Fabrication of bottom electrodes contact pads with Pt. (c) Ion-milling to define active areas (cantilevers or beams). (d) Plasma etching to undercut the Si. Figures are adapted from Ref. [65].

**Fig. 13.** (a) PMN–PT cantilever profile as a function of voltage. The inset is the scanning electron microscopy (SEM) image of PMN–PT cantilever. (b) Tip displacement of the 34 µm long cantilever vs. applied DC voltage. The thick dotted line is the simulation result for a PMN–PT cantilever with the same geometry. The thin dotted line is the modeled result for an electrostatic cantilever with comparable geometry. Figures are adapted from Ref. [65].

**Fig. 14.** (a) RHEED intensity oscillations of LAO films on annealed TiO$_2$-terminated STO/Si substrates. Inset shows the schematic diagram of the LAO/STO heterostructure on the Si substrate. The LAO/STO heterointerfaces were atomically controlled, either (LaO)$^r$-(TiO$_2$)$_2$ or (AlO$_2$)$^r$-(SrO)$_2$. (b) AFM images of three unit cell LAO films on annealed TiO$_2$-terminated STO/Si substrates. Figures are adapted from Ref. [94].

procedures [77]. The conductivity of 2DEG was controlled by induce-polarization switching in the LAO layer [90]. It was demonstrated that 2DEG at LAO/STO can be used as optical and chemical sensors [91, 92]. In order to integrate such unique properties into devices, epitaxial STO on Si offers an ideal platform to grow epitaxial LAO layers. However, there are several obstacles to forming 2DEG at the LAO/STO interface. First, it is crucial to control the termination of STO to generate 2DEG; the heterointerface between LAO and TiO2-terminated STO (TiO2-STO) exhibited metallic 2DEG behavior, whereas the heterointerface between LAO and SrO-terminated STO (SrO-STO) showed insulating behavior [76]. Second, the STO platform should have high crystalline quality: the defects, such as dislocations in STO, strongly degraded the transport property of 2DEG by scattering carriers [83]. Third, the strain state of LAO/STO has to be in the appropriate regime: 2DEG disappeared under more than 1.0% of the tensile strain, while it could survive up to 1.5% of the compressive strain [93]. Therefore, satisfying these requirements is the first step in fabricating STO/Si.

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To investigate the interface and defect structures of the LAO/STO heterostructure on Si, 5 nm thick LAO films on as-grown and annealed TiO2-terminated STO/Si were studied by TEM. Fig. 15a shows a cross-sectional high angle annular dark field (HAADF) image of the heterostructure grown on post-treated STO/Si. After annealing, the dislocation density of the STO template decreased (Fig. 15b). Fig. 15a also shows that each layer of the heterostructure had a uniform thickness. Planar-view TEM studies of both as-grown and post-treated STO/Si showed that the density of threading dislocations was reduced from $1.5 \times 10^{11} \text{cm}^{-2}$ to $8.9 \times 10^{10} \text{cm}^{-2}$. Moiré fringes were observed in the thick areas of the planar-view samples due to the overlap between STO and Si substrate (Fig. 15c and d). Moiré fringes showed discontinuities at threading dislocations (which have a Burgers vector of either [100] or [110] of STO) and changes in spacing and orientation due to the lattice distortion induced by dislocations in STO. In the as-grown STO film, the threading dislocations showed a uniform distribution and a serious lattice distortion was observed (Fig. 15c). On the other hand, the dislocations in the post-treated sample showed

Fig. 16. (a) Temperature dependence of (a) sheet resistance, (b) carrier concentration and (c) mobility of the heterointerface between unpatterned 10 unit cell LAO and TiO$_2$-terminated STO on Si (squares). The STO layer on the Si substrate without the LAO layer showed highly insulating behavior, indicating that the measured transport properties of LAO/STO on Si originated only from 2DEG. For comparison, the electrical transport properties of unpatterned 10 unit cell LAO on the STO single crystal were also measured (circles). (d) LAO thickness dependence of sheet resistance of the unpatterned LAO/STO heterointerface on Si. Figures are adapted from Ref. [94].

Fig. 17. (a) Schematic diagram of the writing process used to generate conducting nanostructures at the LAO/TiO$_2$-terminated STO heterointerface. (b) Electrical conductance between two electrodes during c-AFM writing with $V_{tip} = +4$ V. As the c-AFM tip reached the second electrode, the conductance increased abruptly. The c-AFM tip traveled along the x-direction, as noted in the figure, with a speed of 400 nm s$^{-1}$, relative to the structure. (c) Schematic diagram of the erasing process by cutting the nanowire generated in the writing process. (d) As the c-AFM tip biased at $-4$ V scans crossed the nanowire, the conductance decreased drastically. The c-AFM tip traveled with a speed of 10 nm s$^{-1}$ along the y-direction, as indicated. The width of the nanowire presented in the inset was quantified by fitting the erase curve with a function $G(x) = G_0 - G_1 \tanh(x/h)$ with the best fit parameters: $G_0 = 0.40$ nS, $G_1 = 0.44$ nS and $h = 6.0$ nm. The deconvolved differential conductance $(dG/dx)^{-1}$ is shown in red and has a half-width maximum of 6.9 nm (+4 V wire). Figures are adapted from Ref. [94].

Table 1
Nano-writing capabilities of the heterointerfaces between three unit cell LAO and various STO templates on Si substrates. Only the heterointerface between LAO and post-annealed TiO$_2$-terminated STO/Si exhibited the reversible conductivity switching behavior of the 2DEG nanowire. Table is from Ref. [94].

<table>
<thead>
<tr>
<th>STO surface termination</th>
<th>SrO termination</th>
<th>TiO$_2$ termination</th>
<th>Uncontrolled termination</th>
</tr>
</thead>
<tbody>
<tr>
<td>Post-annealing</td>
<td>As-grown</td>
<td>Annealed</td>
<td>As-grown</td>
</tr>
<tr>
<td>Nano-writing capabilities</td>
<td>No</td>
<td>No</td>
<td>Yes</td>
</tr>
<tr>
<td></td>
<td>As-grown</td>
<td>Annealed</td>
<td>As-grown</td>
</tr>
<tr>
<td></td>
<td>No</td>
<td>No</td>
<td>Annealed</td>
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...a relatively low density and a non-uniform distribution, which resulted in large regions with almost perfect structures and orientation surrounded by “boundaries” formed by dislocations (Fig. 15d). This result indicates that the structural quality of STO films was improved by thermal annealing with a 30% reduction of the density of the threading dislocations. In addition, the atomic structure of the LAO/STO interface was studied by sub-angstrom scanning transmission electron microscopy. The HAADF image in Fig. 15e shows that the LAO film is coherently grown on the post-treated STO/Si with an atomically sharp interface (the positions of the atomic columns are indicated by circles).

It is remarkable that the room-temperature properties are comparable to those for the heterointerfaces between LAO and STO bulk single crystals [76, 94]. The temperature dependence of the sheet resistance, carrier concentration and mobility of an unpatterned heterointerface between ten-unit-cell LAO and post-treated STO/Si by the Van der Pauw method are shown in Fig. 16a–c. We believe that the 2DEG at the LAO/STO heterointerface on Si is useful for room-temperature nanoelectronic devices. The low-temperature mobility, however, was lower than the LAO/STO single crystal. This might be due to the high density of threading dislocations in post-treated STO/Si. The critical thickness of the four unit cells was also observed, as shown in Fig. 16d, which was the same as LAO on the STO bulk single crystals. Larger sample-to-sample variations of the 2DEG property on the LAO/post-treated STO/Si were also observed due to the non-uniform distribution of defects.

The LAO/post-treated STO/Si structure has an advantage over LAO on bulk STO single crystals in that it can lower the voltage to turn the 2DEG conductivity on and off. The nano-writing experiments were done on the three-unit-cell-thick LAO/post-treated STO/Si substrate, a thickness just below the critical thickness for the onset of conduction. The heterointerface conductance was modulated locally using a c-AFM tip that was scanned in contact mode across the LAO surface [77]. A conducting 2DEG nanowire was created by scanning the c-AFM tip along the $x$-axis with a tip potential of $V_{tip} = +4$ V (Fig. 17a). When the c-AFM tip reached from one to the other electrode, an abrupt jump in current was observed (Fig. 17b). After writing the nanowire, the tip was repositioned, as shown in Fig. 17c, biased negatively ($V_{tip} = -4$ V) and scanned slowly along the $y$-direction. When the tip reached the nanowire, the conductance abruptly reached zero again (Fig. 17d). An analysis of the sharpness of the cutting profile provided a measure of the nanowire width, which in this case was $w \sim 6.9$ nm. The minimum voltage required for creating a nanowire was 2.5 V, which was slightly smaller than the counterpart on bulk STO [75]. The existence of a conducting backplane (the Si substrate) may have helped with the writing process when the heterointerface was initially highly insulating. The width of a typical wire written with a $+6$ V c-AFM tip bias was also comparable to the width of a wire written with $V_{tip} = +10$ V on a 3 uc LAO/STO. These results were reproducible with multiple cycles of writing and erasing, and with another set of electrodes. As summarized in Table 1, the nano-writing capability of the three-unit-cell-thick LAO on various STO templates on Si substrates directly determined the quality of the STO template layer on Si. Reversible conductivity switching of nanowire generated at the LAO/STO heterointerface directly on Si offers the possibility of integration with Si for a variety of ultra-high-density nanoelectronic applications.

6. Conclusion

We have reviewed several examples of the epitaxial integration of multifunctional oxide thin films on the Si substrate, which covers multiferroic BFO for magnetoelectric and ferroelectric memory, giant piezoelectric PMN–PT for piezoelectric MEMS, and 2DEG at the LAO/STO interface for oxide nanoelectronics. They maintain high crystalline quality and their own functionalities are comparable to those grown on single-crystal oxide substrates. The effects of defects and thermal strain on the physical properties of oxide thin films imposed by STO/Si substrate, which are specifically discussed in each model system in this review. The oxide heterostructures on the Si substrate are able to provide a tool to explore the physical properties of oxide films, which was not possible with films on single-crystal oxide substrates. Moreover, using a Si substrate allows for the fabrication of strain-free oxide membranes with enhanced physical properties and permits the transferring of epitaxial oxide thin films to any type of flexible platform. It is remarkable that the interfacial effect of oxides and the bulk effect were realized on the Si substrate, which requires precisely stoichiometric and moderately strained STO with an atomically smooth and TiO$_2$-terminated surface.

The MBE-grown epitaxial STO template layer on Si plays a key role not only in bridging two different research
fields of oxides and semiconductors, but also in converting newly discovered physics into device technology. We expect that the quality of epitaxial STO films on Si would be further enhanced with the development of thin film deposition techniques. Beyond just a template, STO itself can be used as a functional layer on Si. Polar [9, ferroelectric [13,95] and relaxor [96] behaviors were observed in epitaxial STO films on various substrates according to the strain and interface states. Moreover, chemical doping with Nb5+ and La3+ allows for controlling of the electrical conductivity of STO from insulator to metal. For an alternative to STO, it is necessary to search for new perovskite oxides as a template on Si. For example, in order to reduce misfit threading dislocations, a multi-layer template with grading lattice parameters would be necessary.

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References

