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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 $SrTiO_3$ (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 $LaAlO_3$ (LAO)/$SrTiO_3$ (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 SiO_2. 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

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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 SiO_2 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 SiO_2 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 $SrTiO_3$ 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 SiO_2 layer. The lattice parameter of Si was 5.3407 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 TiO_2 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 ($\sim 9 \times 10^{-6}\ K^{-1}$) and Si ($\sim 2.5 \times 10^{-6}\ K^{-1}$).

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, $\alpha < 0.05°$). 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 TiO_2-terminated surface of an annealed STO template. In particular, the atomically smooth TiO_2-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 $SrRuO_3$ 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. $SrRuO_3$ (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