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Mechanism of the sequential interface structures changes in the epitaxial Pt/ZrO₂/Si

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The epitaxial growth of functional oxide thin films on Si is generally difficult due to the presence of a native oxide layer and large lattice mismatch. In this study, we elucidate the heteroepitaxial growth fundamental mechanism of a Pt/ZrO₂ epitaxial multilayer buffer structure on Si(111) and Si(001) substrates using X-ray diffraction and atomic-resolution transmission electron microscopy. At the ZrO₂/Si interface, epitaxial growth of ZrO₂ is achieved through an amorphous SiO₂ layer via interfacial reactions and elemental intermixing. ZrO₂{111} facets form on Si(001), reflecting surface energy minimization. At the Pt/ZrO₂ interface, a Pt₃Zr-containing reaction layer forms, enabling epitaxial growth of Pt by mediating interfacial compatibility. This interfacial alloy layer acts as an adaptive interfacial template for structural accommodation. The technique is scalable to 6 and 8 inch wafers, providing a practical platform for multilayer heteroepitaxy. © 2026 The Author(s). Published on behalf of The Japan Society of Applied Physics by IOP Publishing Ltd

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1. Introduction

Heteroepitaxy in inorganic solid materials¹⁾ has played a central role in the advancement of nanometer-scale materials science, particularly in the semiconductor industry. The epitaxial growth of functional materials on Si wafers is highly effective for achieving both high integration density and enhanced functionality in semiconductor devices. Lead zirconate titanate: Pb(Zr,Ti)O₃ (PZT), a representative piezoelectric material, exhibits excellent piezoelectric properties and has been widely employed in a variety of devices, including frequency filters, sensors, transducers, resonators, and MEMS devices.²⁾ These devices have been extensively implemented across diverse fields such as telecommunications, healthcare, and the automotive industry, forming a critical foundation of modern technology. In recent years, driven by the rapid expansion of IoT and 5G communications, the demand for high-performance and miniaturized piezoelectric devices has increased significantly, and their importance is expected to further grow in beyond-5G and 6G technologies.³⁾ In piezoelectric thin films, a high piezoelectric response is achieved when an electric field is applied parallel to the polarization direction or along a direction with a fixed angle relative to it. Consequently, if the film is not epitaxially well aligned, the polarization directions become non-uniform, leading to a reduction in the effective piezoelectric coefficient and degradation of device performance.

Silicon substrates are considered highly attractive for piezoelectric devices due to their abundant availability, low cost, and excellent compatibility with established semiconductor fabrication technologies. However, the presence of a native oxide layer (SiO₂) on the Si surface and interfacial diffusion processes significantly hinder the epitaxial growth of piezoelectric oxides.^{4,5)} As a result, compared with single-crystal oxide substrates such as SrTiO₃ and (LaAlO₃)_{0.3}(Sr₂AlTaO₆)_{0.7}, achieving epitaxial growth of

piezoelectric oxides on Si remains a technologically challenging issue. To overcome these limitations, the introduction of buffer layers, such as SrTiO₃, has been extensively explored to promote epitaxial growth on Si substrates.^{5, 6, 7, 8)} In contrast to optical or electronic applications that utilize single-crystal oxide substrates, ferroelectric capacitor applications require the growth of perovskite oxides on conductive bottom electrodes. In particular, to achieve high ferroelectric performance in PZT, it is essential to realize epitaxial or at least highly oriented growth on electrode materials that are structurally compatible with the perovskite lattice. Various electrode materials, including Pt, Ir, Ru, Cu, RuO₂, IrO₂, YBa₂Cu₃O_{7-δ}, La_{2-x}Sr_xCuO₄, and SrRuO₃ (SRO), have been investigated as substrates for PZT growth.⁵⁾ Among these, Pt is the most widely used electrode material in ferroelectric capacitor structures due to its relatively small lattice mismatch with PZT and its chemical inertness to oxygen. However, Pt does not grow epitaxially directly on Si, as silicide formation readily occurs at the interface.⁹⁾ Therefore, the insertion of adhesion layers or buffer layers between Si and Pt is required to achieve high-quality oriented or epitaxial Pt films.¹⁰⁾ In such heterostructures, precise control of lattice matching and interfacial diffusion remains a critical challenge.

To achieve atomic-level integration of materials with different crystal structures, lattice constants, and thermal expansion coefficients on Si, precise engineering of interfaces, through buffer layer design, growth temperature control, and stress relaxation mechanisms, is indispensable to ensure interfacial compatibility. A thorough understanding of interfacial crystallographic matching mechanisms is therefore essential. Recently, a technique has been reported in which epitaxial Pt thin films are formed on Si substrates via a ZrO₂ buffer layer, demonstrating its effectiveness as a growth template for functional oxide thin films.¹¹⁾ Such Pt/ZrO₂/Si multilayer structures can be fabricated at wafer scales of 6 and 8 inches (Fig. S1, Supplementary data),



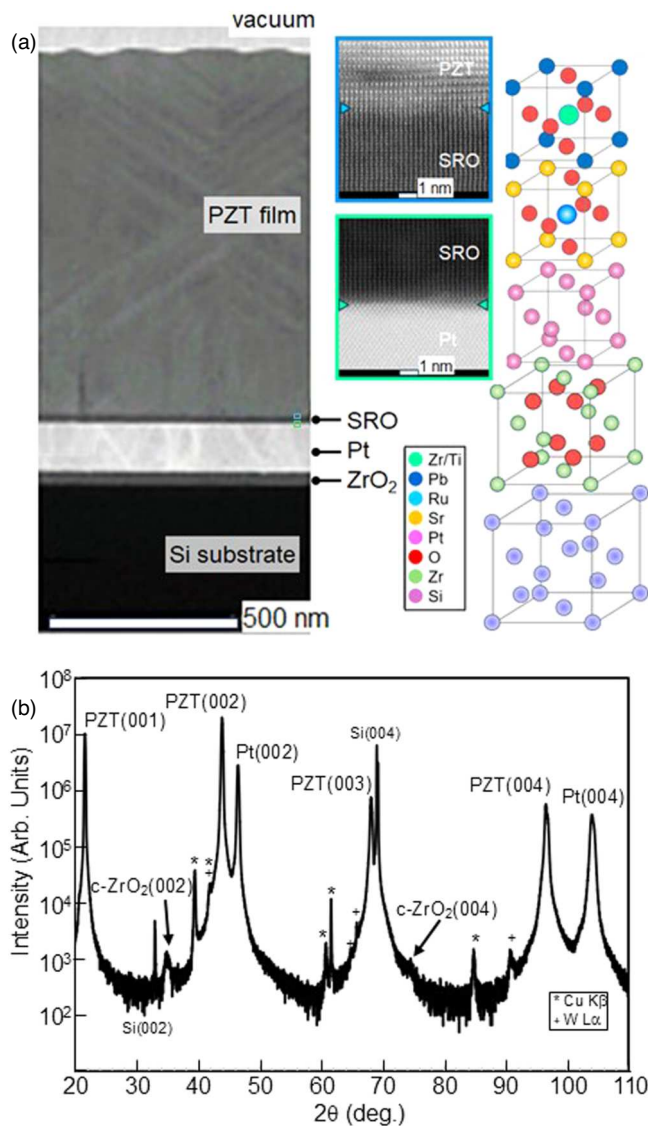


Fig. 1. (a) Cross-sectional STEM images of the PZT thin-film multilayer epitaxial structure fabricated on a Si(001) substrate. A low-magnification image (left) is shown together with high-resolution STEM images of the PZT/SRO interface (upper center) and the SRO/Pt interface (lower center), where the interfaces are indicated by $\blacktriangleleft$. Crystal structure models corresponding to each layer (from bottom: Si, c-ZrO₂, Pt, SRO, and PZT) are also overlaid, with relative dimensions scaled according to their lattice constants. The incident electron beam direction is parallel to [110]_{Si}, and all observations were performed at room temperature. (b) Typical 2θ-ω XRD profile of a representative sample using a Cu X-ray source.

indicating their potential as practical platform technologies. The Pt films exhibit excellent thermal stability and serve as high-quality templates and electrodes. Furthermore, epitaxial growth of perovskite SRO electrode layers on top of Pt enables subsequent epitaxial growth of PZT thin films (Fig. 1). Thus, the Pt/ZrO₂/Si multilayer heteroepitaxial structure provides a viable platform for the growth of functional oxide thin films. However, in this structure, the crystal structure of the ZrO₂ layer is not uniform along the growth direction; instead, compositional and structural variations occur near both the ZrO₂/Si and Pt/ZrO₂ interfaces, facilitating epitaxial growth.¹²⁾ In addition, ZrO₂ is known to grow anisotropically along specific crystallographic directions, forming pyramid-like faceted structures on Si(001) substrates. In general, for heterointerfaces with

large lattice mismatch, domain matching epitaxy (multi-epitaxy), in which integer multiples of lattice spacings are matched across the interface, can reduce the effective lattice mismatch.¹³⁾ However, in the Pt/ZrO₂ system, not only the lattice constants but also the crystal structures and bonding characteristics differ significantly, and the establishment of epitaxial growth at the ZrO₂/Pt interface cannot be fully explained within the framework of conventional lattice matching or domain matching alone. In particular, how structural variations and compositional modulation near the interface contribute to crystal growth remains unclear, and a detailed understanding of the interfacial structure and growth mechanism is still lacking.

Heteroepitaxy is not merely a thin-film growth technique, but a powerful strategy for extracting intrinsic material properties and enabling novel functionalities. In this study, we focus on the Pt/ZrO₂/Si multilayer structure and perform systematic analyses centered on atomic-resolution transmission electron microscopy (TEM). We elucidate the structural evolution and formation of interfacial reaction layers, and propose a new mechanism for multilayer heteroepitaxial growth based on sequential atomic redistribution and structural rearrangement. Our results reveal that ZrO₂ undergoes stepwise structural transformations on the nanometer scale at both the Si and Pt interfaces, thereby enabling the formation of a coherent multilayer epitaxial structure. The insights obtained in this study are of significant academic importance and provide a fundamental basis for enabling epitaxial growth of functional materials on Si, offering new design guidelines for heterogeneous material integration and next-generation device architectures.

2. Experimental methods

First, the 6 or 8 inch silicon wafer (commercial, mirror-polished) with a naturally oxidized surface was used as the substrate. No intentional oxide removal or surface treatment was performed immediately prior to ZrO₂ deposition. A ZrO₂ layer with a thickness of approximately 40 nm was deposited over the entire surface via electron beam evaporation. The base pressure of the vacuum chamber was maintained below 1×10^{-3} Pa, and O₂ gas was introduced stepwise during deposition to promote oxidation. The wafer temperature was maintained at 500°C throughout the deposition. Next, a Pt layer was deposited on the ZrO₂ layer using DC sputtering with a target size of $\phi 250$ mm. The deposition conditions included a substrate temperature of 450°C–600°C, an Ar gas pressure of 0.1 Pa, and an applied power of 100 W, with a typical film thickness of 150 nm. The PZT thin film was deposited on a Pt/ZrO₂/Si multilayer buffer following the growth of an ~10 nm SRO layer. The growth of both SRO and PZT was carried out using radio frequency sputtering.

The crystallinity of the thin-film samples was evaluated by X-ray diffraction (XRD, SmartLab, Rigaku) using 2θ-ω and φ-scan measurements. Cross-sectional TEM and scanning TEM (STEM) observations were conducted at room temperature (RT) using two transmission electron microscopes (JEM-ARM 200 F, JEOL and HD-2700, Hitachi High-Tech). STEM observation with complementary energy-dispersive X-ray spectroscopy (EDS) elemental mapping was also performed at RT (JEM-ARM 200 F NEOARM, JEOL).

The TEM samples were prepared by protecting the film surface with adhesive, followed by standard mechanical polishing and focused ion beam (FIB, Helios 650, Thermo Fisher Scientific, or FB2200, Hitachi High-Tech) processing. XRD and TEM observation were conducted at RT. The crystal structure models shown in this study were generated using the VESTA software.¹⁴⁾

3. Results and discussion

3.1. Multilayer buffer architecture for epitaxial PZT thin films

Figure 1(a) shows the cross-sectional high-angle annular dark-field (HAADF)-STEM image of the PZT film grown on a multilayer buffer stack formed on a Si(001) substrate. The buffer layers were fabricated using our proprietary process, and the PZT film was subsequently grown on top of this stack. The HAADF-STEM image clearly reveals four stacked layers, ZrO₂, Pt, SRO, and PZT, sequentially deposited on the Si substrate, each exhibiting clear and atomically smooth interfaces and forming a well-defined heterostructure. High-magnification TEM images of the PZT/SRO and SRO/Pt interfaces further confirm that PZT, SRO, and Pt share coherently aligned atomic arrangements, indicating the formation of high-quality epitaxial interfaces.

Figure 1(b) presents the XRD 2θ - ω scan of the multilayer structure. In addition to the strong Si(004) substrate peak at $2\theta = 69.12^\circ$, broad peaks corresponding to cubic ZrO₂ (c-ZrO₂) 002 and 004 appear at $2\theta = 35.08^\circ$ and 74.53° , respectively. Peaks corresponding to Pt(002) and Pt(004) are observed at $2\theta = 46.45^\circ$ and 104.18° , together with distinct peaks from PZT(001), (002), (003), and (004) at $2\theta = 21.46^\circ$, 43.75° , 68.08° , and 96.53° , respectively. Although the SRO layer is thinner than 10 nm and therefore does not produce a clearly discernible XRD peak, the combined evidence from cross-sectional STEM confirms that the PZT(001)/SRO(001)/Pt(001)/ZrO₂(001) stack is epitaxially grown on Si(001). A similar epitaxial relationship was also confirmed on Si(111), where PZT(111)/SRO(111)/Pt(111)/ZrO₂(111) was obtained.

Achieving epitaxial PZT films requires adequate matching of both lattice parameters and crystal structures within the buffer stack. As summarized in Table I, Si with a diamond structure ($a = 0.543$ nm) serves as the substrate, and a cubic ZrO₂ layer (c-ZrO₂, fluorite structure, $a = 0.509$ nm) is grown first to provide a lattice constant reasonably close to that of Si, thereby enabling a coherent initial epitaxial template. Subsequently, fcc Pt ($a = 0.392$ nm) is deposited on ZrO₂, acting not only as a functional electrode but also as a lattice-matching template for subsequent layers. Introducing perovskite-structured SRO (pseudo-cubic $a_{pc} = 0.396$ nm) on Pt ensures lattice compatibility with Pt

while providing a crystallographic bridge to the perovskite PZT layer. Finally, perovskite PZT ($a_{pc} = 0.405$ nm) is grown on SRO, resulting in a highly oriented, high-quality epitaxial PZT film. In addition to lattice matching, the multilayer design also accounts for thermal expansion compatibility and adequate interlayer adhesion, both of which are essential for device-level mechanical stability and long-term reliability. Overall, achieving heteroepitaxial growth of PZT requires a stepwise buffer stack in which lattice parameters and crystal structures are carefully matched from the substrate to the functional layer. Through such optimized multilayer buffer engineering, high-quality single-crystal PZT thin films can be reliably formed. The stepwise matching of lattice parameters and crystal structures across the buffer layers: from the substrate to the uppermost film, is supported by the Pt/ZrO₂ bilayer grown on the Si substrate, which serves as the fundamental platform for the epitaxial growth of all subsequent layers. In the following section, we focus on this Pt/ZrO₂/Si structure and discuss in detail the crystal growth behavior and the lattice accommodation mechanisms at the ZrO₂/Si and Pt/ZrO₂ interfaces.

3.2. Pt/ZrO₂/Si epitaxial multilayer buffer structure

Figure 2 shows the 2θ - ω scans and ϕ -scan results of the Pt/ZrO₂ multilayer buffer films fabricated on Si(111) and Si(001) substrates. To verify the epitaxial relationship, the ϕ -scan measurements were performed using the diffraction peaks of Si(110), c-ZrO₂(110), and Pt(110) for both substrate orientations. From the 2θ - ω scans, the out-of-plane crystal orientations were identified as Pt(111)/c-ZrO₂(111) on Si(111) [Fig. 2(a)] and Pt(001)/c-ZrO₂(001) on Si(001) [Fig. 2(c)]. In the ϕ -scans, six peaks reflecting the threefold symmetry of the (111) plane were observed in Fig. 2(b), whereas four peaks reflecting the fourfold symmetry of the (001) plane were observed in Fig. 2(d). These results confirm that the epitaxial orientation relationships are Pt(111)[110]/c-ZrO₂(111)[110]/Si(111)[110] and Pt(001)[100]/c-ZrO₂(001)[100]/Si(001)[100].

When c-ZrO₂ and Pt grow epitaxially with the orientation relationships Pt(111)[110]/c-ZrO₂(111)[110] and Pt(001)[100]/c-ZrO₂(001)[100], the lattice mismatch estimated simply from the lattice constants listed in Table I is as large as approximately -23% in the case of one-to-one matching. In general, the lattice mismatch tolerable for epitaxial growth is only a few percent.^{15,16)} When this range is greatly exceeded, the critical thickness predicted by the Matthews–Blakeslee model approaches zero, making elastically coherent epitaxial growth essentially impossible.^{17,18)} Moreover, when lattice matching cannot be maintained, many systems exhibit disordered growth or polycrystallization.^{19,20)} However, in practical heteroepitaxial systems, lattice accommodation does not necessarily occur in a one-to-one manner. Instead, domain

Table I. Crystal information. Crystallographic data are taken from the International Centre for Diffraction Data (ICDD) Powder Diffraction File (PDF) database. a_{pc} denotes the pseudo-cubic lattice constant.

Material	Crystal structure	Space group (Space number)	Lattice constant (nm)	PDF No.
Pb(Zr _{0.52} Ti _{0.48})O ₃	Perovskite (tetragonal)	P4mm (99)	$a_{pc} = 0.405$	01-070-6602
SrRuO ₃	Perovskite (orthorhombic)	Pnma (62)	$a_{pc} = 0.396$	01-083-6490
Pt	FCC	Fm $\bar{3}$ m (225)	$a = 0.392$	00-072-0455
cubic-ZrO ₂	Fluorite	Fm $\bar{3}$ m (225)	$a = 0.509$	01-072-2742
Si	Diamond	Fd $\bar{3}$ m (227)	$a = 0.543$	01-086-4266

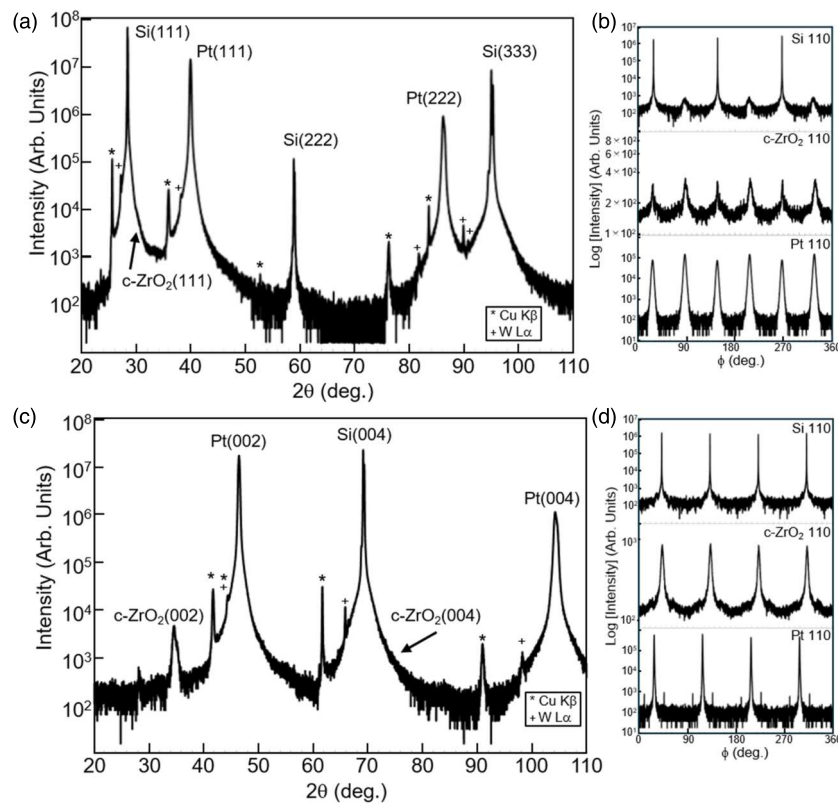


Fig. 2. XRD results of the Pt/ZrO₂ epitaxial multilayer buffer structures fabricated on (a), (b) Si(111) and (c), (d) Si(001) substrates. (a), (c) show the 2θ - ω diffraction profiles, and (b), (d) show the ϕ scans for the (110) reflections of Si, ZrO₂, and Pt. All measurements were performed at room temperature using a Cu X-ray source.

matching (i.e. multi-epitaxy), in which integer multiples of lattice spacings are matched across the interface, can significantly reduce the effective lattice mismatch.¹³⁾ For the present system, for example, a 9:7 matching between Pt and c-ZrO₂ yields an effective mismatch of approximately 1%, which falls within the typical tolerance for epitaxial growth. Nevertheless, a well-defined epitaxial relationship is experimentally observed between Pt and c-ZrO₂ in this system, indicating that additional interfacial mechanisms beyond conventional lattice matching play a critical role in accommodating the mismatch. To clarify the origin of this epitaxial relationship despite the large differences in crystal structure and bonding nature between Pt and c-ZrO₂ crystal, we focused on the atomic-scale structure of the interface and investigate the crystallographic matching mechanism through detailed TEM observations.

3.3. ZrO₂/Si interface structure

Figures 3(a) and 4(a) show cross-sectional TEM images of Pt/ZrO₂ multilayer buffer structures fabricated on Si(111) and Si(001) substrates, respectively. It is confirmed that ZrO₂ and Pt thin films are sequentially stacked on the Si substrates. A notable feature is that epitaxial growth is not achieved through perfectly abrupt heterointerfaces, but rather is mediated by the formation of interfacial reaction layers at each interface. Focusing first on the ZrO₂/Si interface, an amorphous SiO₂ layer with a thickness of several nanometers is observed on both Si(111) and Si(001) substrates. On top of this layer, epitaxial ZrO₂(111) [Fig. 3(b)] and ZrO₂(001) [Fig. 4(b)] films are formed, respectively. In general, amorphous SiO₂ lacks long-range order and therefore cannot serve as a template for epitaxial growth based on conventional lattice matching. Accordingly, the formation of well-

oriented epitaxial ZrO₂ films on an amorphous SiO₂ layer appears, at first glance, contradictory. Nevertheless, such growth behavior has been reported previously. For example, oriented growth of ZrO₂ and yttria-stabilized zirconia (YSZ) has been demonstrated on Si(001) substrates with native oxide layers, where high-quality epitaxial films are obtained despite the presence of an amorphous SiO₂ interlayer.^{7,21,22, 23,24)} Furthermore, first-principles calculations have shown that the stability and electronic structure of the interface vary significantly depending on the atomic configuration and termination, indicating that the interface can adopt multiple chemically distinct states rather than a single well-defined structure.²⁵⁾ In addition, at the ZrO₂/Si interface, it has been reported that the growth of a SiO₂-like interfacial layer and the formation of a composite bilayer structure (ZrSi_xO_y/SiO_x) occur depending on the oxygen partial pressure and annealing conditions. These observations indicate that diffusion processes, including Si indiffusion and grain-boundary diffusion, play a crucial role in the formation of the interfacial layer.²²⁾ Furthermore, oxygen tracer studies have shown that ZrO₂ can actively supply oxygen to the Si substrate during annealing, leading to the growth of a relatively thick interfacial SiO₂ layer even under conditions where bare Si would exhibit different oxidation kinetics.²³⁾ This suggests that oxygen diffusion through the ZrO₂ layer and subsequent oxygen injection into Si significantly contribute to interfacial layer formation.

The thermodynamic stability of ZrO₂ plays a key role in understanding this phenomenon. The standard Gibbs free energy of formation (ΔG) of ZrO₂ is approximately $-1040 \text{ kJ mol}^{-1}$, which is more negative than that of SiO₂

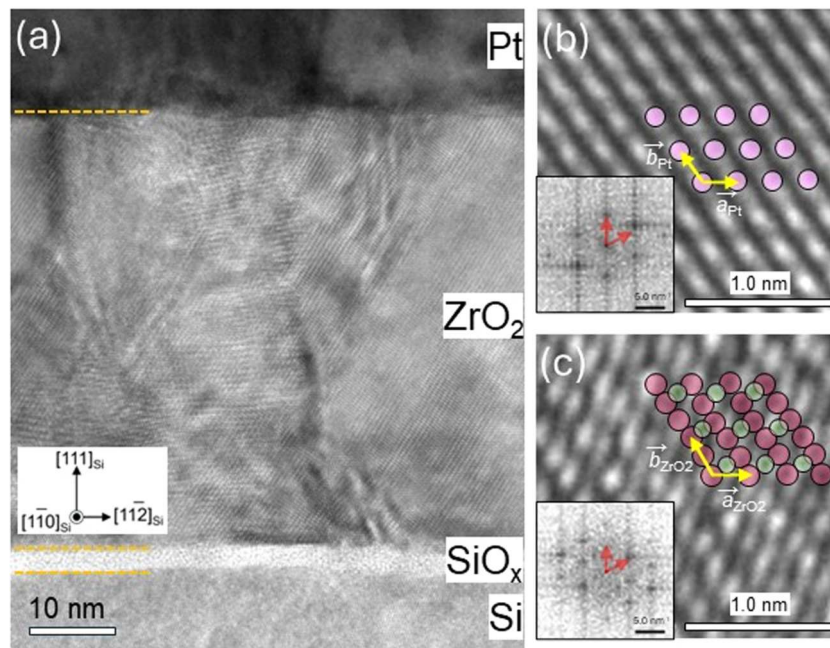


Fig. 3. (a) Cross-sectional TEM image of the Pt/ZrO₂/Si buffer structure fabricated on a Si(111) substrate, acquired at room temperature. Yellow dashed lines are included as guides to indicate the positions of the SiO_x/Si, ZrO₂/SiO_x, and Pt/ZrO₂ interfaces. (b) Atomic-resolution cross-sectional TEM image of the Pt layer and (c) that of the ZrO₂ layer, with their corresponding FFT images (insets). Atomic structure models along the $(\bar{1}10)$ plane and unit vectors (yellow arrows) are overlaid on the TEM images, and the corresponding unit vectors (red arrows) are also overlaid on the FFT images.

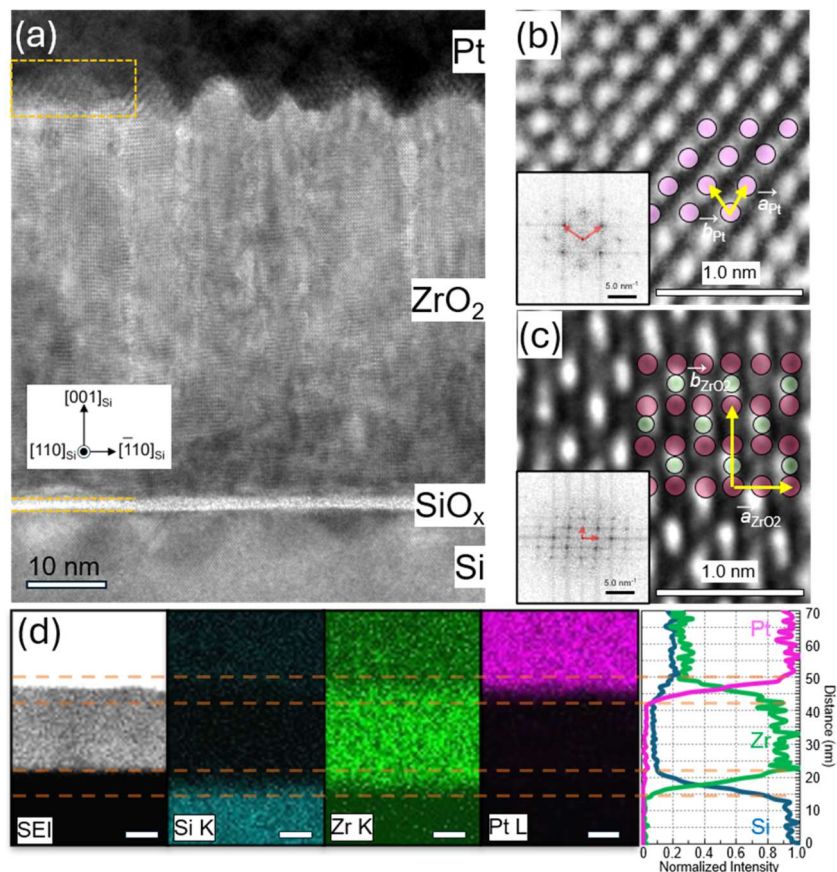


Fig. 4. (a) Cross-sectional TEM image of the Pt/ZrO₂/Si buffer structure fabricated on a Si(001) substrate, acquired at room temperature. Yellow dashed lines and box are included as guides to indicate the positions of the SiO_x/Si, ZrO₂/SiO_x, and Pt/ZrO₂ interfaces. (b) Atomic-resolution cross-sectional TEM image of the Pt layer and (c) that of the ZrO₂ layer, with their corresponding FFT images (insets). Atomic structure models along the $(\bar{1}10)$ plane and unit vectors (yellow arrows) are overlaid on the TEM images, and the corresponding unit vectors (red arrows) are also overlaid on the FFT images. (d) STEM-EDS analysis of an independently prepared cross-sectional specimen with the same Pt/ZrO₂/Si(001) multilayer configuration, showing the SEI image, elemental intensity maps of Si K (blue), Zr K (green), and Pt L (pink), together with the corresponding normalized elemental intensity profiles obtained by integrating the mapped region. Scale bars in (d) correspond to 5 nm.

(approximately -800 kJ mol^{-1}).²⁶⁾ This indicates that ZrO_2 is thermodynamically more stable, suggesting that even if local chemical reactions occur at the SiO_2 interface during deposition, the formation of the ZrO_2 phase is energetically favored. Indeed, the interfacial reaction behavior at the ZrO_2/Si interface is known to strongly depend on the deposition method and growth conditions. For instance, ZrO_2 films deposited by atomic layer deposition can exhibit relatively abrupt interfaces with minimal interdiffusion across the SiO_2 layer.²¹⁾ In contrast, under high-energy growth conditions such as pulsed laser deposition, dynamic interfacial processes have been reported during the initial stages of growth, including decomposition of SiO_2 , desorption of SiO , and formation of Zr-O networks.⁷⁾ These results indicate that the amorphous SiO_2 layer should not be regarded as a passive buffer, but rather as a dynamic interfacial region that can undergo partial decomposition, reconstruction, and chemical reactions during film growth. In the present study, high-resolution TEM observations reveal localized regions at the interface where Zr and Si are intermixed, suggesting the occurrence of atomic mixing or interfacial reactions. Such reactions are likely to facilitate the nucleation of ZrO_2 and influence the early stages of crystal growth. Therefore, even on an amorphous SiO_2 layer, a thermodynamically stable ZrO_2 phase can form through local interfacial reactions and atomic rearrangements. On the other hand, the emergence of a well-defined crystallographic orientation is likely associated with the polymorphic nature of ZrO_2 . ZrO_2 is a polymorphic material that exhibits multiple crystal phases, including monoclinic, tetragonal, and cubic structures, whose stability depends on temperature, stress, and dopant incorporation.^{27,28)} Since these phases possess different lattice parameters and surface energies, nuclei with orientations that minimize the interfacial energy may be selectively stabilized and grow preferentially during the initial stage of growth. Such an orientation-selection process provides a plausible explanation for the formation of an epitaxial ZrO_2 film even on an amorphous SiO_2 layer. The growth behavior observed here is considered to be fundamentally different from remote epitaxy, in which crystallographic information is transmitted through atomically thin intermediate layers such as graphene.²⁹⁾ Instead, the present results suggest an epitaxial growth mechanism in which crystallographic orientation is established through interfacial reactions and atomic rearrangements at the amorphous SiO_2 interface.

3.4. $\text{ZrO}_2\{111\}$ surfaces

At the Pt/ZrO_2 interface, a clear difference is observed between films grown on $\text{Si}(111)$ and $\text{Si}(001)$ substrates. The surface of the ZrO_2 film formed on the $\text{Si}(111)$ substrate is flat [Fig. 3(a)], and the topmost surface is confirmed to be the $\text{ZrO}_2(111)$ plane. In contrast, the ZrO_2 film grown on the $\text{Si}(001)$ substrate exhibits a faceted surface structure composed of inclined planes with heights of approximately 5–10 nm [Fig. 4(a)]. These facets are inclined by approximately 55° with respect to the surface normal, indicating that they correspond to $\text{ZrO}_2\{111\}$ planes. The facets observed in Fig. 4(a) mainly correspond to the $(\bar{1}11)$ and $(1\bar{1}1)$ planes. SEM observations confirm that four equivalent $\{111\}$ facets, including $(\bar{1}\bar{1}1)$ and (111) , are formed in addition

to $(\bar{1}11)$ and $(1\bar{1}1)$. The formation of $\{111\}$ facets on the surface of epitaxial ZrO_2 films with the orientation relationship $\text{ZrO}_2(001)[100]//\text{Si}(001)[100]$ strongly suggests that the $\text{ZrO}_2(111)$ plane possesses high surface stability.

The formation of $\{111\}$ facets can be attributed to the anisotropy of the surface energy of ZrO_2 . In general, for fluorite-structured oxides, the (111) plane is known to be the most stable surface with the lowest surface energy. In contrast, the (001) plane is a polar surface, which is thermodynamically unstable due to the intrinsic charge imbalance under ideal conditions.^{30–32)} Such polar surfaces are known to be stabilized through surface reconstruction, step formation, or decomposition into lower-energy facets. Therefore, the formation of $\{111\}$ facets in $\text{ZrO}_2(001)$ -oriented films can be understood as an energy minimization process that alleviates the instability of the polar (001) surface by exposing the energetically favorable (111) planes. This tendency is also supported by first-principles calculations for ZrO_2 and cubic YSZ, and similar behavior has been reported for fluorite-type oxides such as CeO_2 , where high-energy surfaces reconstruct into $\{111\}$ facets upon annealing.²⁷⁾ These results indicate that the observed $\{111\}$ faceted structure originates from the intrinsic crystallographic and thermodynamic properties of ZrO_2 .

The formation of the faceted structure is considered to be closely related to surface diffusion and surface reconstruction processes during film growth. Under high-temperature growth conditions, surface diffusion is enhanced, leading to the progressive formation of faceted structures that minimize the surface energy at early growth stages or during film thickening, after which the morphology is preserved during subsequent growth.³³⁾ In addition, atomic rearrangement during the post-deposition cooling process may further promote reconstruction toward the more stable $\{111\}$ surfaces. During this reconstruction process, competition arises among surface energy reduction, surface energy anisotropy, step energy, and surface diffusion length. Although facet formation reduces the overall surface energy, the creation of facet boundaries incurs an energy cost, and the characteristic length scale is determined by the balance among these competing factors. Such mechanisms are widely recognized as a general framework for crystal growth and surface morphology evolution, and the facet size of approximately 5–10 nm observed in this study is therefore considered to be governed by the energy balance associated with surface energetics and diffusion during growth.

Furthermore, the EDS elemental maps shown in Fig. 4(d) reveal that the spatial distributions of Zr and Pt are not completely separated near the Pt/ZrO_2 interface, resulting in a broadened compositional transition region. Such elemental distributions partly reflect the three-dimensional morphology of the interface arising from the $\{111\}$ faceted structure described above. On the other hand, the observed elemental broadening cannot be explained solely by geometrical effects and also suggests the occurrence of elemental interdiffusion and interfacial reactions at the Pt/ZrO_2 interface. In addition, the sequential high-resolution TEM and FFT analyses shown in Fig. S2 (Supplementary data) indicate that the ordered ZrO_2 crystal structure is preserved throughout the ZrO_2 layer and that the structural modification is localized near the Pt/ZrO_2 interface.

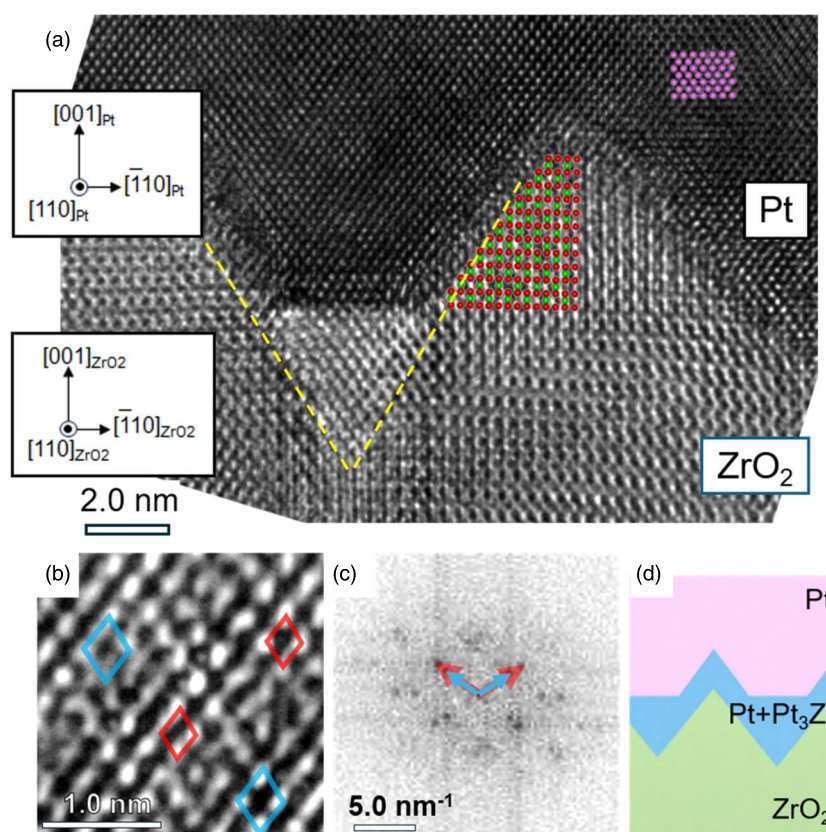


Fig. 5. (a) Atomic-resolution cross-sectional TEM image of the Pt/ZrO₂ interfacial region on a Si(001) substrate. The formation of an interfacial reaction layer is observed at the base of the pyramidal ZrO₂ surface. Yellow dashed lines are included as guides to indicate part of the ZrO₂ interface. Crystal lattice models of ZrO₂ and Pt are overlaid on the image. (b) Cross-sectional TEM image of the interfacial reaction layer region acquired from the same viewing direction as in (a), and (c) the corresponding FFT image. In addition to the lattice fringes (red diamonds) and reciprocal lattice spots (red arrows) corresponding to fcc-Pt, additional lattice fringes (blue diamonds) and reciprocal lattice spots (blue arrows) corresponding to an expanded fcc-like lattice are observed, indicating the coexistence of Pt and Pt₃Zr-like lattice regions. (d) Schematic illustration of the interfacial structure derived from the cross-sectional TEM analysis.

3.5. Pt/ZrO₂ interfacial reaction layer

Figure 5(a) shows a cross-sectional atomic-resolution image of the Pt/ZrO₂ interface formed on a Si(001) substrate. As described above, the ZrO₂ surface exhibits a pyramidal structure composed of {111} facets. At the bottom of these inclined facets, a layer with a crystal structure different from both ZrO₂ and Pt is formed. This interfacial reaction layer exists with a thickness of approximately 2–3 nm from the base of the pyramid, and fcc-structured Pt is observed to grow epitaxially on top of this layer [Fig. 5(b)]. The presence of this interfacial reaction layer is also consistent with the EDS elemental maps shown in Fig. 4(d). At the Pt/ZrO₂ interface, the Pt concentration increases abruptly toward the film surface, whereas the Zr concentration decreases gradually toward the Pt layer, suggesting the existence of a Zr-rich region near the interface. FFT analysis of this Zr-rich interfacial region reveals, in addition to the diffraction spots corresponding to fcc Pt [Fig. 5(c), red arrows], additional diffraction spots originating from a structure that retains the same crystallographic symmetry but possesses a lattice periodicity expanded by approximately 1.35 times [Fig. 5(c), red arrows]. This result indicates the presence of a new crystalline phase with an enlarged lattice constant of approximately 0.53 nm while preserving the fcc framework, suggesting a structural change that cannot be explained by simple elastic strain.

Considering both the existence of the Zr-rich Pt–Zr mixed region and the appearance of an fcc-like phase with an expanded lattice periodicity, the formation of a Pt–Zr interfacial reaction phase is strongly suggested. Although several intermetallic compounds have been reported in the Pt–Zr binary system, Pt₃Zr is particularly noteworthy because it is an ordered intermetallic compound based on an fcc Pt framework and is known to possess a larger lattice constant than pure Pt.³³⁾ The Zr-rich elemental distribution and the fcc-like crystal structure with an expanded lattice parameter observed in the present study are in good agreement with the characteristics of Pt₃Zr. On the other hand, the interfacial reaction layer observed here is confined to a local region only a few nanometers thick, and TEM observations suggest that it is not a single-phase Pt₃Zr layer but rather a coexistence region of Pt₃Zr-like and Pt domains. This interpretation is also consistent with the monotonic compositional variation observed by EDS. Therefore, the interface is better understood not as a distinct intermediate layer but as a transition region in which Pt₃Zr and Pt coexist while the composition and crystal structure evolve continuously [Fig. 5(d)]. Furthermore, the fcc-like lattice image shown in Fig. 5(b) and the FFT pattern in Fig. 5(c) appear while preserving the crystallographic orientation of Pt, suggesting a probable orientation relationship of Pt(001)[100]/Pt₃Zr(001)[100] within the interfacial reaction region.

Based on the structural analyses and their consistency with previous studies, the Pt–Zr reaction phase observed in this work is interpreted as a transition region where Pt_3Zr and Pt lattices coexist. In addition, first-principles calculations have reported the structural stability of Pt_3Zr and the electronic states associated with the formation of Pt/ZrO₂ interfaces,³⁴⁾ which is consistent with the formation of the fcc-like interfacial reaction layer observed in this study. Furthermore, strong interfacial interactions involving oxygen vacancies and charge redistribution have been reported at Pt/ZrO₂ interfaces, promoting Pt–Zr bond formation and interfacial structural rearrangement.³⁵⁾ These considerations suggest that the formation of this Pt_3Zr phase is not merely a byproduct of interfacial reactions, but is considered to originate from the energetic requirement to reduce the interfacial free energy at the Pt/ZrO₂ interface. In fact, c-ZrO₂ and Pt grow epitaxially with the orientation relationships $\text{Pt}(111)[110]//\text{c-ZrO}_2(111)[110]$ and $\text{Pt}(001)[100]//\text{c-ZrO}_2(001)[100]$, for which a naive one-to-one comparison of the lattice parameters gives a large nominal mismatch of approximately -23% . On the other hand, considering a possible domain-matching-type correspondence (e.g. 9:7), the effective mismatch could be reduced to approximately 1%. However, even in such a case, the large differences in crystal structure and bonding nature between c-ZrO₂ and Pt make it difficult to fully explain the observed high-quality epitaxial relationship solely in terms of simple lattice matching. Therefore, the minimization of interfacial energy must be achieved not only through the reduction of lattice mismatch, but also through the simultaneous relaxation of discontinuities in bonding states, coordination environments, and chemical composition. From this perspective, the Pt_3Zr phase should be regarded not merely as a geometrical bridge for lattice matching, but as an energetically favorable intermediate state that mediates local discontinuities in bonding, coordination, and chemistry at the interface.

Furthermore, the reaction layer observed in this study is formed as a nanoscale transition region in which Pt_3Zr and Pt lattices coexist. Although the detailed spatial distribution of the Pt_3Zr and Pt lattices within the reaction layer remains unclear at present, the entire layer appears to constitute a transition region characterized by gradual compositional and structural variations. Since Zr is supplied from the ZrO₂ side toward the interface, Pt–Zr reaction phases containing Zr are formed near the interface, whereas the Zr concentration decreases with increasing distance from the interface, eventually leading to a Pt-dominated region [Fig. 4(d)]. Therefore, the reaction layer is considered to function as a region that mediates the structural and chemical transition from ZrO₂ to Pt. Such a compositional gradient indicates that structural and chemical reconstruction at the interface proceeds in a spatially localized manner. Consequently, the structural evolution observed near the interface is considered to reflect the Zr concentration distribution and the corresponding local changes in thermodynamic stability. Interestingly, the formation of a reaction layer in which Pt_3Zr and Pt lattices coexist was also confirmed at Pt/ZrO₂ interfaces formed on Si(111) substrates. This result suggests that epitaxial growth mediated by an interfacial reaction layer represents a general growth mode that is not limited to a specific substrate orientation. In contrast to the faceted

ZrO₂ surface observed on Si(001), the ZrO₂ layer on Si(111) exhibits a relatively flat ZrO₂(111) surface, resulting in a smaller spatial extent of the interfacial reaction layer (Fig. S3, Supplementary data). This difference can be attributed to the surface geometry: on Si(111), the ZrO₂ surface is terminated by a single (111) orientation with a well-defined surface normal, whereas on Si(001), the formation of {111} facets creates intersecting ridge structures that generate pocket-like regions at the facet boundaries, where interfacial reactions are locally enhanced. As a result, a more spatially extended interfacial reaction layer is formed on Si(001).

The Pt_3Zr phase retains an fcc-like framework while incorporating Zr atoms, thereby forming a mixed bonding state based on strong electronic hybridization between Pt and Zr.²⁶⁾ Such a bonding configuration, together with charge redistribution and bond rearrangement at the interface,³⁶⁾ is considered to provide an intermediate character that mediates between the Zr–O bonding in ZrO₂ and the metallic bonding in Pt. As a result, a gradual reconstruction of the local atomic arrangement can occur over a few nanometers, enabling effective redistribution of misfit strain and reduction of interfacial free energy despite the large nominal lattice mismatch. Therefore, the interfacial accommodation should be interpreted not as a continuous change in lattice constant, but as a spatially localized and gradual reorganization of local coordination and bonding states, driven by interdiffusion, alloy formation, and electronic interactions.^{35–37)} The preservation of crystallographic orientation across the interface despite such interfacial structural reconstruction indicates that the observed growth should not be regarded as merely oriented growth, but rather as an epitaxial growth process mediated by interfacial reactions. In this sense, the Pt_3Zr -containing interfacial reaction layer functions as an adaptive template that establishes the local structural and chemical environment required for the subsequent epitaxial growth of Pt.

Epitaxial accommodation via the formation of an interfacial intermediate layer has also been reported in other systems with large symmetry differences and lattice mismatch. For example, in the bronze-phase VO₂/SrTiO₃ system, a nanoscale interfacial bilayer is formed between the substrate and the film, which structurally bridges two crystallographically dissimilar materials and enables epitaxial growth.³⁸⁾ This phenomenon is interpreted as a self-templating mechanism, in which the interface reconstructs itself to serve as a template for subsequent growth. A similar concept has been reported for ferroelectric Hf_{0.5}Zr_{0.5}O₂(111) films grown on La_{2/3}Sr_{1/3}MnO₃(001), where epitaxial growth is achieved despite a large nominal lattice mismatch, and the interface is governed by local domain matching and structural rearrangement rather than simple one-to-one lattice correspondence.³⁹⁾ These results indicate that epitaxial growth in highly mismatched systems can be realized not by direct lattice matching, but through local structural reconstruction, domain-wise matching, or the formation of intermediate phases.

In the present system, the Pt_3Zr interfacial layer can therefore be understood as a self-adaptive intermediate phase that mediates structural and chemical discontinuities between ZrO₂ and Pt, while providing a template for epitaxial growth. Furthermore, in Pt/ZrO₂ systems, interdiffusion of Zr and

alloying with Pt, as well as charge transfer and bond rearrangement at the interface, have been reported.³⁸⁾ These electronic interactions are expected to contribute to the stabilization of the interfacial alloy phase.

Such interfacial reactions and diffusion processes promote alloy formation through the supply of Zr from the ZrO₂ side, leading to a self-organized reconstruction of the interfacial structure. Therefore, the formation of the Pt₃Zr-containing interfacial layer at the Pt/ZrO₂ interface can be understood as the result of a synergistic interplay of (i) interfacial chemical reactions driven by the formation of Pt–Zr reaction phases, (ii) electronic stabilization associated with Pt–Zr hybridization and charge redistribution, and (iii) structural reconstruction that redistributes misfit strain and reduces interfacial free energy. Consequently, the Pt₃Zr-containing interfacial reaction layer observed in this study can be regarded as an adaptive template that alleviates the structural and chemical discontinuities between ZrO₂ and Pt while providing the local structural and chemical environment necessary for subsequent epitaxial growth.

4. Conclusions

In this study, the heteroepitaxial growth mechanism of a Pt/ZrO₂ multilayer buffer structure formed on Si(111) and Si(001) substrates was systematically investigated by XRD and atomic-resolution TEM. At the ZrO₂/Si interface, epitaxial growth of ZrO₂ was achieved through an amorphous SiO₂ layer via interfacial reactions, elemental intermixing and structural rearrangement. In addition, the formation of ZrO₂{111} facets on the ZrO₂ surface was observed, indicating surface stabilization driven by surface energy minimization. At the Pt/ZrO₂ interface, a Pt₃Zr-containing interfacial reaction layer was formed, and this self-adaptive interfacial layer enables epitaxial growth by gradually relaxing the large lattice mismatch between ZrO₂ and Pt. These findings demonstrate that sequential elemental redistribution and structural rearrangement at the interfaces play an essential role in establishing multilayer heteroepitaxial growth.

The self-adaptive crystallographic accommodation mechanism mediated by the interfacial reaction layer revealed in this study is considered to be of high generality and provides an important guideline for realizing epitaxial growth even in hetero-material systems with large lattice mismatch. Furthermore, this technique is applicable at the 6 and 8 inch wafer scale and, as a platform technology directly relevant to industrial applications, enables the epitaxial growth of functional material thin films and provides a useful guideline for heterogeneous integration and next-generation device design toward beyond 5G and 6G.

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- 1) V. L. Tassev, *Crystals* **7**, 178 (2017).
- 2) G. L. Smith et al., *J. Am. Ceram. Soc.* **95**, 1777 (2012).
- 3) T. Guo, J. Chen, Y. Wen, C. Lin, S. Zhang, J. Ding, and N. Wang, *Adv. Mater. Technol.* **11**, e01772 (2026).
- 4) Y. Zhu, P. Yan, T. Yi, L. Cao, and L. Li, *Surf. Interface Anal.* **27**, 972 (1999).
- 5) N. Izyumskaya, Y.-I. Alivov, S.-J. Cho, H. Morkoç, H. Lee, and Y.-S. Kang, *Crit. Rev. Solid State Mater. Sci.* **32**, 111 (2007).
- 6) E. Tokumitsu, K. Itani, B.-K. Moon, and H. Ishiwaru, *Jpn. J. Appl. Phys.* **34**, 5202 (1995).
- 7) Y. Wang et al., *Appl. Phys. Lett.* **80**, 97 (2002).
- 8) N. Wakiya, K. Shinozaki, and N. Mizutani, *J. Ceram. Soc. Jpn.* **110**, 358 (2002).
- 9) J.-R. Chen, T.-S. Heh, and M.-P. Lin, *Surf. Sci.* **162**, 657 (1985).
- 10) K. Meinel, A. Eichler, S. Förster, K.-M. Schindler, H. Neddermeyer, and W. Widdra, *Phys. Rev. B* **74**, 235444 (2006).
- 11) Japan Patent No. 7011760 (2021).
- 12) Japan Patent No. 7527658 (2024).
- 13) M. J. Lee, C. B. Eom, and D. G. Schlom, *Cryst. Growth Des.* **12**, 1000 (2012).
- 14) K. Momma and F. Izumi, *J. Appl. Crystallogr.* **44**, 1272 (2011).
- 15) E. A. Fitzgerald, *Mater. Sci. Rep.* **7**, 87 (1991).
- 16) R. Hull and J. C. Bean, *Crit. Rev. Solid State Mater. Sci.* **17**, 507 (1992).
- 17) J. W. Matthews and A. E. Blakeslee, *J. Cryst. Growth* **27**, 118 (1974).
- 18) J. W. Matthews and A. E. Blakeslee, *J. Vac. Sci. Technol.* **14**, 989 (1977).
- 19) M. A. Choudhary, J. Kundin, and H. Emmerich, *Comput. Mater. Sci.* **83**, 481 (2014).
- 20) T. Zheleva, K. Jagannadham, and J. Narayan, *J. Appl. Phys.* **75**, 860 (1994).
- 21) M. Copel, M. Gribelyuk, and E. Gusev, *Appl. Phys. Lett.* **76**, 436 (2000).
- 22) A. S. Foster, F. Lopez Gejo, A. L. Shluger, and R. M. Nieminen, *Vacuum* **82**, 847 (2008).
- 23) S. Ferrari and G. Scarel, *J. Appl. Phys.* **96**, 144 (2004).
- 24) T. Ohmi, T. Imaoka, and K. Sugiyama, *Thin Solid Films* **217**, 125 (1992).
- 25) P. W. Peacock, K. Xiong, K. Y. Tse, and J. Robertson, *Phys. Rev. B* **73**, 075328 (2006).
- 26) NIST-JANAF Thermochemical Tables, <https://janaf.nist.gov/>.
- 27) D. R. Mullins, *Surf. Sci. Rep.* **70**, 42 (2015).
- 28) R. C. Garvie, R. H. Hannink, and R. T. Pascoe, *Nature* **258**, 703 (1975).
- 29) B.-I. Park, J. Kim, K. Lu, X. Zhang, S. Lee, J. M. Suh, D.-H. Kim, H. Kim, and J. Kim, *Nano Lett.* **24**, 2939 (2024).
- 30) A. Christensen and E. A. Carter, *Phys. Rev. B* **58**, 8050 (1998).
- 31) C. Noguera, *J. Phys. Condens. Matter* **12**, R367 (2000).
- 32) J. Noguera, *J. Phys. C: Solid State Phys.* **12**, 4977 (1979).
- 33) H.-C. Jeong and E. D. Williams, *Surf. Sci. Rep.* **34**, 171 (1999).
- 34) L. Zhang, Y. Wang, Z. Liu, X. Zhang, and J. Wang, *RSC Adv.* **7**, 54772 (2017).
- 35) X. Zhang, W. H. Butler, and A. G. Petukhov, *Phys. Rev. B* **74**, 235444 (2006).
- 36) Y. Chen, S. Zhang, and X. Yang, *Surf. Interfaces* **52**, 104871 (2024).
- 37) S. Peng, R. Li, Y. Huang, Y. Zhang, J. J. Cao, and S. Lee, *Appl. Surf. Sci.* **600**, 154056 (2022).
- 38) X. Gao, S. Lee, J. Nichols, T. L. Meyer, T. Z. Ward, M. F. Chisholm, and H. N. Lee, *Sci. Rep.* **6**, 38168 (2016).
- 39) S. Estandía, N. Dix, M. F. Chisholm, I. Fina, and F. Sánchez, *Cryst. Growth Des.* **20**, 3801 (2020).