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A prospective submonolayer template structure for integration of functional oxides with silicon

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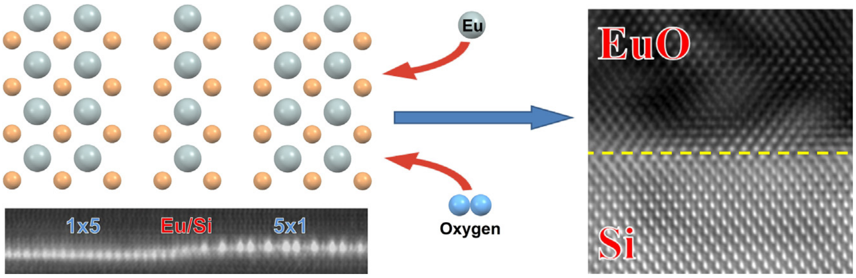
HIGHLIGHTS

- A novel template based on the 1x5 surface reconstruction of Eu protects the interface and promotes oxide growth on silicon.
- The atomic structure of the template supports a high metal coverage necessary for epitaxial coupling of oxides with silicon.
- The advantage of the novel template is demonstrated as coming from suppressed surface oxidation.
- The potential of the new template is exemplified by successful synthesis of the archetypal spintronic system EuO/Si.

GRAPHICAL ABSTRACT



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ABSTRACT

Epitaxial integration of oxides with the ubiquitous silicon technological platform promises devices with dreamed-of functionality but is difficult to achieve due to chemical processes at the Si/oxide interface. The standard approach suggests a protective template – a surface superstructure of $SrSi_2$ stoichiometry; still, only a handful of oxides couple to Si with atomically abrupt interface. We advocate an alternative approach – the use of metal-rich submonolayer templates as a general recipe, in particular, robust 1×5 reconstructions of Sr and Eu on Si. Their fail-safe synthesis is reported, diffraction techniques and electron microscopy reveal the structure and thermal stability of the reconstructions. The surface protection is discussed in terms of oxidation kinetics. The advantages of the new templates are demonstrated recruiting the example of the paradigmatic spintronic system EuO/Si.

1. Introduction

Nowadays, functional oxides are an integral part of electronics and spintronics [1]: their rich physics and multifunctionality inspire new concepts of electronic devices. The surfaces of oxides are especially sensitive to defects and strains, and exhibit properties remarkably different from those of the bulk [2]. Last years have witnessed an explosion of interest in emergent phenomena at oxide interfaces [3]; deliberate creation of novel states at the interfaces shifts focus to the atomic-scale synthesis of epitaxial oxide thin films [4,5]. Integration of functional oxides with silicon is among the most important technological problems [6] since Si is the most advanced device platform. Crystalline oxides on Si exhibit superb bulk properties and enable interface

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phenomena with applications ranging from high-k insulators for MOSFETs [7] to ferroelectric devices [8]. Nowadays, covalent-ionic strontium titanate $SrTiO_3$ on silicon is routinely used as a template/intermediate layer for incorporation of epitaxial oxide films into Si technology [9,10]. However, a quest for new generation devices calls for direct integration of functional oxides with silicon.

Coupling of ionic oxides with covalently bound Si is inherently challenging. It is aggravated by large lattice mismatch, interdiffusion, reduction of oxide by Si, oxide non-stoichiometry, oxidation of Si, variation of the metal oxidation state, *etc.* The challenges are best met with a layer-by-layer deposition approach utilizing MBE [6]. A breakthrough in the growth of crystalline oxides on Si (001) came from employing submonolayer Zintl phases of surface metal silicides as templates [11]. The commonly accepted recipe is based on a superstructure formed by 1/2 monolayer (ML, 1 ML is defined as $6.78 \cdot 10^{14}$ sites/cm^2) of Sr on Si (001) with $SrSi_2$ stoichiometry. This layer is designed to promote epitaxy by preventing Si oxidation; the charge transfer in the template results in the disappearance of the asymmetry of Si dimers [12]. However, relatively low metal content in $SrSi_2$ stoichiometry does not guarantee Si surface from oxidation.

Although the structure of the surface silicide is relatively simple, its formation turns out to be a complex process involving surface migration of Si atoms [13]. A number of possible interfacial structures are discussed, especially for $SrTiO_3$/Si [14–16] and BaO/Si [17,18]. What is most important, deliberate engineering of a structural composition at the interface may serve as a key to tune the electronic properties of the interface layer thus modifying the prospective device's functionality [19,20].

Despite the enormous efforts invested in the epitaxial growth of oxides on Si only a small number of oxides can be grown in a single-crystalline form with an abrupt interface [6], such as γ-Al_2O_3, YSZ, $(La_xY_{1-x})_2O_3$, Sc_2O_3, $SrTiO_3$. All the knowledge aggregated so far on the interfacial structure clearly indicates the central role of the surface reconstruction. Engineering of this surface superstructure may result in templates for the growth which are expected to remarkably affect the outcome. However, to date there is no general recipe for integration of functional oxides into silicon platform. So far, each particular case presents an attempt to grow an oxide on Si using specific surface template. For example, several attempts to grow ferromagnetic semiconductor EuO directly on Si [21–23] employed different templates with significantly different outcome. What is missing is the systematic study of the spatial structure of different reconstructions, the chemical and electrostatic control of the oxide/Si interface, the chemical reactivity of different templates for the growth of different oxides.

Here, we establish Sr and Eu surface reconstructions with high metal content as templates for the growth of functional oxides on Si. In particular, surface superstructures with the 1 × 5 symmetry are studied and set against those with the 1 × 2 symmetry. Their synthesis is robust; they are stable within a wide temperature range. The spatial structure of these reconstructions is determined for the first time with a combination of techniques including diffraction of high- and low-energy electrons and transmission electron microscopy. It is shown that oxidation of the reconstruction goes through an intermediate structure with the same 1 × 5 symmetry. The effect of the novel template is demonstrated by successful growth of the EuO/Si structure with atomically abrupt interface. Such an approach may provide new opportunities for control over interface phase electrodynamics of Si/oxide junctions, which has been previously explored only within the 1 × 2 model [20]. These developments may bridge the gap between the emerging field of complex oxide electronics and the established field of semiconductor devices.

2. Experimental

The surface superstructures are grown in a Riber Compact 12 system for molecular beam epitaxy furnished with a UHV system comprising Gamma Vacuum Titan Ion Pump, cryopump Cryo-Torr 8 (Brooks CTI Cryogenics), a titanium sublimation pump and cryopanels cooled by liquid nitrogen. The pressure of residual gases is less than 10^{-10} Torr. The substrates are high-ohmic compensated Si (001) wafers with miscut angles not exceeding 0.5°. 4 N Sr, 4 N Eu and 5 N Al are supplied from Knudsen cell effusion sources. Molecular oxygen (6 N) flux for the growth of oxides and oxidation studies is tuned with the gas flow system based on the mass flow controller and Baratron manometer. The cell and substrate temperatures are controlled with thermocouples while PhotriX ML-AAPX/090 infrared pyrometer (LumaSense Technologies) measures the absolute temperature of the substrate. Intensity of molecular beams is determined with Bayard-Alpert ionization gauge fitted at the substrate site. The surface of the substrate is controlled *in situ* with RHEED fitted with kSA 400 Analytical RHEED System (k-Space Associates, Inc.).

Separate LEED experiments are carried out in an Omicron UHV system with a base pressure below 10^{-10} Torr. The substrates are P-doped Si (001) wafers. They are carefully outgassed at 600 °C for several hours and subsequently flashed at 1200 °C to remove natural surface oxide. Samples are heated with a direct current while the temperature is measured with infrared pyrometers. Europium flux comes from a home-made W-filament evaporator with a typical deposition rate of 0.5 ML/min, determined with a quartz crystal microbalance.

For the microstructural studies the samples are sectioned in the direction normal to the film surface in a Helios 600 Nanolab (FEI) scanning electron microscope/focus ion beam (FIB) dual beam system equipped with gas injectors and micromanipulator (Omniprobe). To prevent sputtering, 2–3 μm Pt layer is deposited on the sample surface prior to FIB milling procedure with 30 kV Ga^+ ions. The cross-sectional samples of 8 × 5 μm^2 size are attached to an Omniprobe semiring and thinned to the electron transparency by 5 kV and then 2 kV Ga^+ ions. Due to easy oxidation both sides of Sr reconstruction samples are covered with 10 nm protective C layer before removing from the chamber. All samples are studied in BF TEM and HAADF STEM modes in a Titan 80–300 TEM/STEM (FEI) operating at 300 kV and equipped with a spherical aberration (C_s) probe corrector, HAADF detector, an atmospheric thin-window energy dispersive spectrometer (Phoenix System, EDAX) and post-column energy filter (Gatan).

3. Results and discussion

The choice of surface silicide $SrSi_2$ with the 1 × 2 symmetry as a template is straightforward as it corresponds to exact saturation of Si (001) surface dangling bonds. However, the phase diagram of Sr on Si (001) supplies 3 other structures [24]: reconstructions 2 × 3, 1 × 5 and 1 × 3. The change of the surface silicide template may be a powerful technique to engineer the interface. This option calls to be explored. The attempts to grow oxides on the 2 × 3 reconstruction of Sr on Si (with low metal coverage) are unsuccessful [13] because such template is highly reactive due to incomplete saturation of dangling bonds. Oxide growth on different Sr silicide templates is reported for uncomplicated case of lattice-matched $Sr_{0.3}Ba_{0.7}O$ [25] pinpointing the 1 × 5 reconstruction as producing the best results. This surface superstructure is suggested to accommodate larger amount of metal than the common $SrSi_2$ template. The extra metal atoms may provide an additional protection against oxidation. The idea to use a metal-rich reconstruction is somewhat similar in purpose to proposed earlier scheme [11] employing an alkaline earth metal coverage of the silicide at low temperature for its protection from oxygen flux.

To draw a distinction between different templates we synthesized 4 types of surface structures. The first two structures are the 1 × 2 and 1 × 5 reconstructions of Sr on Si (001). The Si surface is prepared by heating the substrate at 950 °C to remove the natural oxide layer. Each Si atom of the surface monolayer has 2 covalent bonds with the bulk and 2 unpaired valences. The atoms become three-coordinated by dimerization producing 2 × 1 and 1 × 2 reconstructions on adjacent Si surface terraces as confirmed by characteristic reflection high-energy