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Epitaxial ferromagnetic oxide thin films on silicon with atomically sharp interfaces

P. de Coux,^{1,2} R. Bachelet,^{1,a)} B. Warot-Fonrose,² V. Skumryev,³ L. Lupina,⁴ G. Niu,⁴ T. Schroeder,⁴ J. Fontcuberta,¹ and F. Sánchez^{1,b)}

¹Institut de Ciència de Materials de Barcelona (ICMAB-CSIC), Campus de la UAB, 08193 Bellaterra, Barcelona, Spain

²CEMES-CNRS, 29 rue Jeanne Marvig, BP 94347, Toulouse Cedex 4, France

³Institució Catalana de Recerca i Estudis Avançats (ICREA), Barcelona, Spain and Dep. de Física, Univ. Autònoma de Barcelona, 08193 Bellaterra, Spain

⁴IHP, Im Technologiepark 25, 15236 Frankfurt (Oder), Germany

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A bottleneck in the integration of functional oxides with silicon, either directly grown or using a buffer, is the usual formation of an amorphous interfacial layer. Here, we demonstrate that ferromagnetic CoFe₂O₄ films can be grown epitaxially on Si(111) using a Y₂O₃ buffer layer, and remarkably the Y₂O₃/Si(111) interface is stable and remains atomically sharp. CoFe₂O₄ films present high crystal quality and high saturation magnetization. © 2014 AIP Publishing LLC.

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Complex oxides, with wide variety of functional properties, are extraordinarily appealing as new materials to improve responses in existing devices, or to develop radically new ones. Indeed, complex oxides are already considered highly relevant emerging materials for the future evolution of microelectronics by the “More than Moore” approach.¹ However, the success of oxide electronics is conditioned by the bottleneck of the difficult integration of complex oxides with silicon. In spite that oxide electronics constitutes one of the most active research fields in materials science and technology, the integration of complex oxides with silicon still requires substantial progress.

The main cause of the difficult integration of crystalline oxides with silicon is the strong chemical interaction.² Most of complex oxides react strongly with silicon, and direct growth of high quality epitaxial films has been found to be possible in only few cases.^{3,4} Thus, buffer layers are generally necessary, being SrTiO₃ or yttria-stabilized zirconia (YSZ) used in most of the cases. These buffers have permitted epitaxial growth with excellent functional properties of relevant oxides including ferroelectric Bi_{3.25}La_{0.75}Ti₃O₁₂ (Ref. 5) and BaTiO₃,^{6–8} piezoelectric Pb(Mg_{1/3}Nb_{2/3})O₃-PbTiO₃,⁹ ferromagnetic manganites,¹⁰ and spinels,¹¹ and high mobility LaAlO₃/SrTiO₃ interfaces.¹² However, the interface between silicon and the SrTiO₃ or the YSZ buffer is not stable under the conditions of high substrate temperature and partial pressure of oxygen required for epitaxy of these functional oxides, and the resulting buffer/silicon interface degrades with formation of an amorphous interfacial layer. This degradation is reported in all examples mentioned above. The stability of the interface is a serious problem in some applications, including field-effect and tunnel devices. For such cases, buffer layers with higher chemical stability with silicon are necessary.

Here, we report on the use of Y₂O₃ as a buffer layer for the epitaxy of ferromagnetic spinel CoFe₂O₄ (CFO) on Si(111). CFO grows by the mechanism of domain matching epitaxy, and presents high crystal quality and high magnetization in spite of the large lattice mismatch of around 21% with Y₂O₃. The Y₂O₃/Si interface is found to be stable and transmission electron microscopy confirms the absence of an interfacial layer.

Y₂O₃ buffer layers were deposited by molecular beam epitaxy on the 7 × 7 reconstructed Si(111). Additional information is reported elsewhere.¹³ The Y₂O₃ buffered Si(111) wafers were cut in small chips and used as substrate to grow CFO films by pulsed laser deposition ($\lambda = 248$ nm, fluence ~ 1.5 J/cm²) at 550 °C substrate temperature. Oxygen pressure was increased progressively until 0.1 mbar as described elsewhere.¹¹ Structural characterization was done by reflection high energy electron diffraction (RHEED), X-ray diffraction (XRD), high resolution transmission electron microscopy (HRTEM) in cross-section geometry along the Si[11–2] zone axis (using a spherical aberration corrected FEI-Tecnai microscope at 200 kV), and atomic force microscopy (AFM) in dynamic mode. Magnetization loops were measured by superconducting quantum interference device (SQUID) magnetometer.

CFO and Y₂O₃ are both cubic with lattice parameters $a_{\text{CFO}} = 8.392$ Å and $a_{\text{Y2O3}} = 10.604$ Å, respectively. The RHEED pattern (Fig. 1(a)) of the Y₂O₃ buffer layer with a thickness (t) of $t = 31$ nm, taken along Si[11–2], shows a high intensity specular spot and Bragg reflections. The intensity decreases immediately as deposition of CFO starts (Fig. 1(b)) and RHEED intensity oscillations were not observed. However, the patterns at the end of the deposition confirmed the epitaxial growth of the film. Figs. 1(c) and 1(d) show the patterns recorded at the end of deposition of the $t = 26$ nm CFO film along Si[11–2] and Si[1–10], respectively. The patterns are streaky, attesting in-plane crystalline order. This observation provides the first indication that the lattice mismatch, f (%) = $100 \times (a_{\text{CFO}} - a_{\text{Y2O3}}) / a_{\text{Y2O3}} \sim -20.9\%$, does not prevent epitaxy. The modulation of the intensity along

^{a)}Permanent address: Institut des Nanotechnologies de Lyon (INL), UMR5270 CNRS, Ecole Centrale de Lyon, 36 avenue Guy de Collongue, 69134 Ecully, France.

^{b)}Author to whom correspondence should be addressed. Electronic mail: fsanchez@icmab.es

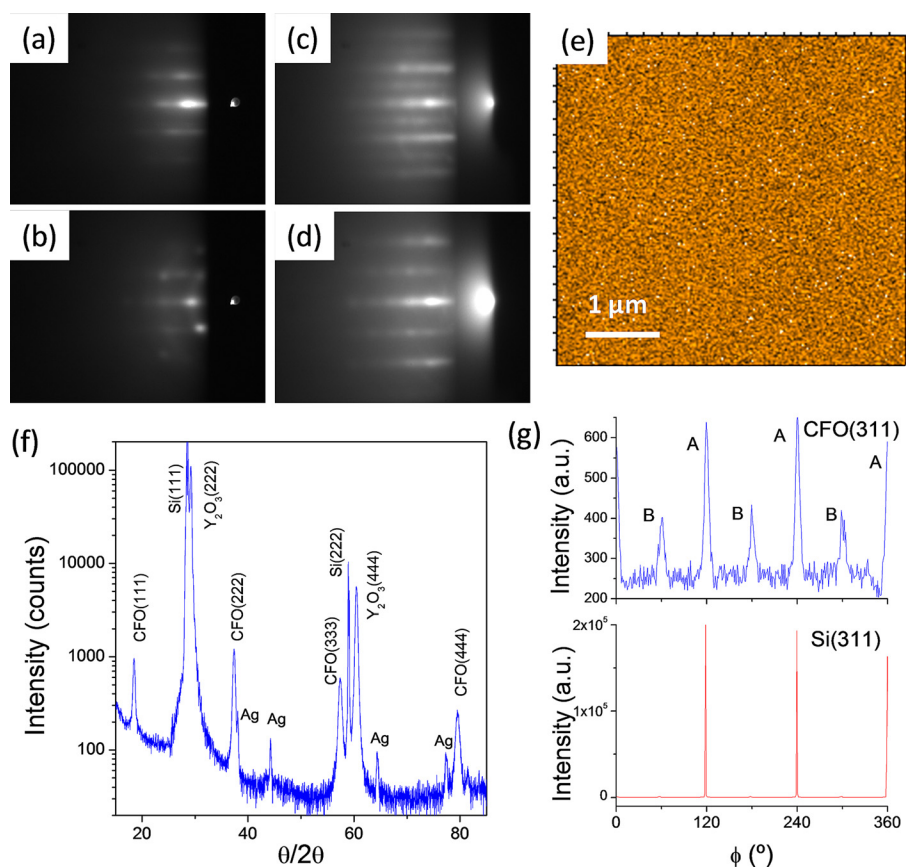


FIG. 1. RHEED patterns taken along the Si[11-2] direction of (a) Y_2O_3 buffer layer, (b) early stage of CFO growth ($t = 2-3 \text{ \AA}$), and (c) at the end ($t = 26 \text{ nm}$) of deposition. (d) RHEED pattern at the end of the deposition along Si[1-10]. (f) XRD $\theta-2\theta$ scan and (g) XRD ϕ -scan around (311) reflections of CFO (top panel) and Si (bottom panel).

the streaks suggests certain film roughness. The AFM image in Fig. 1(e) shows an homogeneous surface with dense granular morphology, being the grain size smaller than 100 nm and the root-mean square (rms) roughness is smaller than 5 Å. The XRD $\theta-2\theta$ scan around symmetrical reflections (Fig. 1(f)) shows (*111*) reflections from Si, Y_2O_3 , and CFO. There are no peaks corresponding to other reflections from CFO or Y_2O_3 (the narrow peaks of smaller intensity correspond to the silver used to glue the substrate, not removed from the lateral sides of the sample). Thus, CFO/ Y_2O_3 /Si(111) is fully (*111*) oriented with absence of spurious crystalline phases. The out-of-plane lattice parameters of CFO and Y_2O_3 are 4.848 Å and 6.122 Å, respectively, coincident with bulk values and thus point to relaxed films structures. The ϕ -scans around (311) reflections of CFO and Si, presented in Fig. 1(g), confirm that the CFO film is epitaxial. There are two sets of three CFO(311) peaks, indicating coexistence of two in-plane

crystal variants. The set with higher intensity, at the same ϕ positions as the Si reflections, is usually known as A-type orientation.¹³ The smaller intensity peaks 60° apart from the A-type set correspond to the same crystal structure of CFO but rotated 180° in the plane and is usually known as B-type orientation. Considering the intensity of both sets of peaks the fraction of minority B variant can be roughly estimated to be around 30%. In contrast, the Y_2O_3 films present a single B-type variant.¹³ Thus, the epitaxial relationships of the A and B type CFO crystal variants respect Y_2O_3 and Si correspond, respectively, to $[11-2]\text{CFO}(111)/[-1-12]\text{Y}_2\text{O}_3(111)/[11-2]\text{Si}(111)$, and $[-1-12]\text{CFO}(111)/[11-2]\text{Y}_2\text{O}_3(111)/[11-2]\text{Si}(111)$.

The epitaxy mechanisms of CFO on Y_2O_3 and the sharpness of CFO/ Y_2O_3 and Y_2O_3 /Si interfaces have been investigated by TEM. In Fig. 2(a), we present a HRTEM image around the CFO/ Y_2O_3 interface (marked by arrows). Both

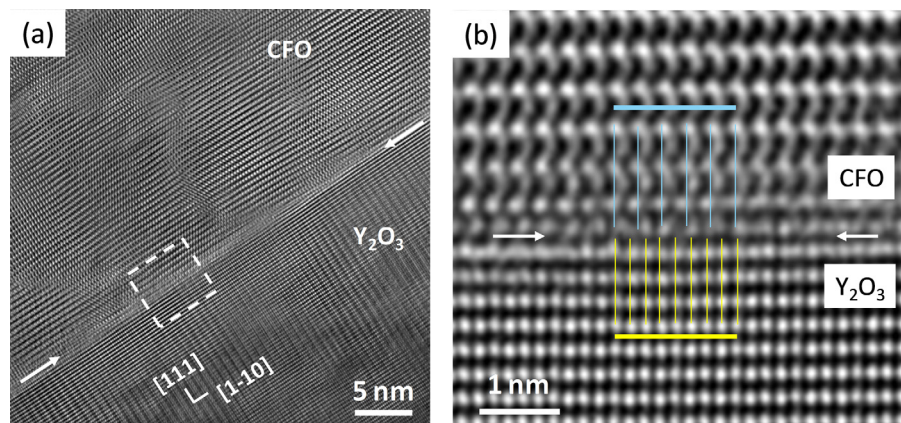


FIG. 2. (a) Cross section HRTEM image along $[11-2]$ zone axis around the CFO/ Y_2O_3 interface. The arrows mark the interface. (b) Zoom of the region marked in (a). Yellow and light blue vertical lines mark Y_2O_3 and CFO planes, respectively. The domain length is indicated by the horizontal lines.

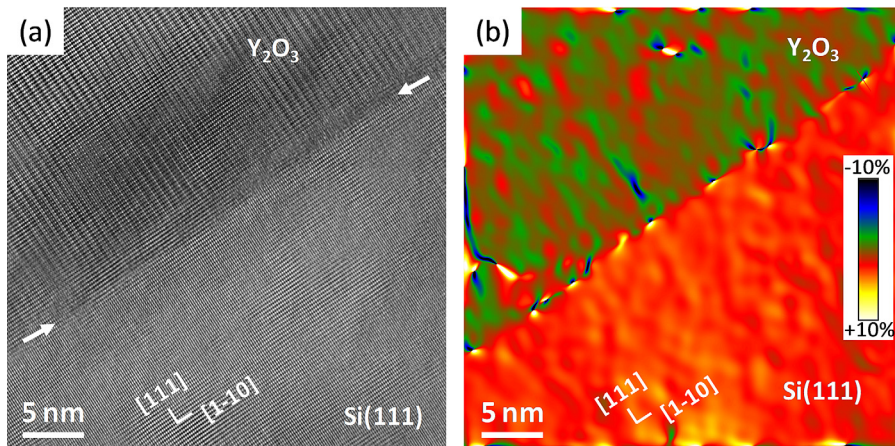


FIG. 3. (a) Cross section HRTEM image along $[11-2]$ zone axis around the $\text{Y}_2\text{O}_3/\text{Si}$ interface. The arrows mark the interface. The corresponding map of the in-plane strain of Y_2O_3 with respect to Si is in (b).

layers are homogeneous and present high structural quality, without signs of chemical interaction or incoherent areas at the interface. The absence of disorder is remarkable considering the large lattice mismatch. The region around the interface marked with the dashed line in Fig. 2(a) is zoomed in Fig. 2(b). Vertical lines (light blue for planes in CFO and yellow for planes in Y_2O_3) are drawn to visualize better the epitaxy. It is appreciated that five planes in CFO match with eight lattice planes in Y_2O_3 , according with the so called *domain matching epitaxy* mechanism.¹⁴ The domain formed by the 5 atomic planes of CFO is 14.84 Å long and the one with 8 planes of Y_2O_3 15.0 Å, being the mismatch of only around -1.1% , permitting epitaxy. A similar mechanism of domain matching epitaxy has been also observed in CFO films on $\text{Sc}_2\text{O}_3/\text{Si}(111)$.¹⁵

A HRTEM image around the $\text{Y}_2\text{O}_3/\text{Si}(111)$ interface is shown in Fig. 3(a). The interface, marked by arrows, is very abrupt and without any interfacial layer. The absence of an interfacial layer was confirmed in all regions analyzed by HRTEM. The sharpness of the $\text{Y}_2\text{O}_3/\text{Si}(111)$ interface had been already reported,¹³ and our results prove that it is stable after deposition of the CFO film. This is an outstanding result since the interface between a crystalline oxide and Si usually degrades under the conditions required for subsequent epitaxial growth of complex oxides. Indeed, a SiO_x interfacial layer was present in CFO/ $\text{Sc}_2\text{O}_3/\text{Si}(111)$ samples.¹⁵ The sharpness of the $\text{Y}_2\text{O}_3/\text{Si}(111)$ interface is also evident in the corresponding map of the in-plane strain of

Y_2O_3 with respect to Si (Fig. 3(b)), determined using as reference a zone of the silicon substrate and obtained by geometrical phase analysis.¹⁶ It indicates a homogeneous strain around -2.4% which corresponds to full relaxation of Y_2O_3 . Also, some interfacial dislocations shown by local deformation fields are well visualized.

Figure 4 shows a magnetization loop measured at 10 K with the field applied in the plane of the sample, along the Si $[1-10]$ direction. The shrinking at low fields is characteristic of magnetization loops of ferromagnetic spinel film.¹⁷⁻¹⁹ The saturation magnetization is around 320 emu/cm^3 , slightly lower than the bulk value of around 400 emu/cm^3 and similar to the magnetization of CFO films grown on perovskite substrates.^{18,20}

In summary, Y_2O_3 buffer layers permit epitaxial integration of spinel ferromagnetic CFO with Si(111). CFO grows epitaxially in spite of the huge lattice mismatch above 20%. It occurs by the mechanism of domain matching epitaxy and suggests opportunities of integration of other functional oxides with silicon by using highly mismatched buffer layers. The interface between Y_2O_3 and Si(111) is stable and remains atomically sharp after CFO deposition. It points to high potential of ultrathin CFO/ Y_2O_3 bilayers for fabrication of spintronic tunnel devices.

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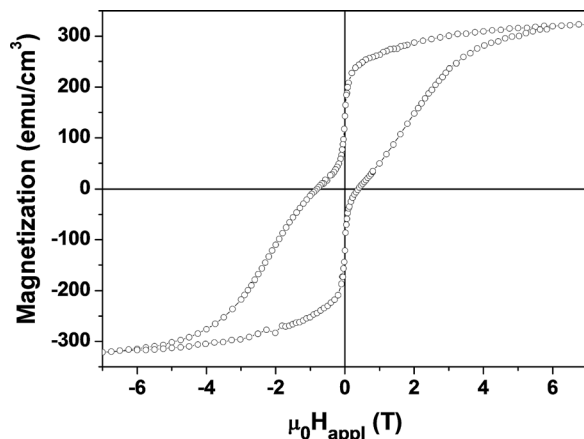


FIG. 4. Magnetization loop at 10 K with the field applied in-plane of the film, along Si $[1-10]$.

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