

Supporting Data

Oxygen Vacancy-Mediated Epitaxy: TiO₂(111)/Al₂O₃(0001) and Ferromagnetic Cr₂O₃(0001)/TiO₂(111)

C. Ladewig, F. Anwar and J. A. Kelber

Dept. of Chemistry, University of North Texas, Denton, TX 76203

S. Q. A. Shah and P. A. Dowben

Dept. of Physics and Astronomy, University of Nebraska-Lincoln, Lincoln, NE 68588

Titanate thin films are of broad and increasing interest in applications ranging from photocatalysis [1, 2] to advanced microelectronics and spintronics [3, 4]. These applications frequently involve scaling of oxide thicknesses to < 10 nm, often with significant departures from bulk structures and properties. Generally, TiO₂(100) orientation (rutile or anatase) is observed for growth on Al₂O₃(0001) by various growth methods, although the formation, by PLD, of a Ti₂O₃(111) interphase ~ 1 nm thick has been reported, but with subsequent formation of rutile TiO₂(001) at greater thicknesses [5].

We report here the growth, by MBE, of 5 nm thick stoichiometric TiO₂(111) films on Al₂O₃ with lattice constants and structure of Ti₂O₃(111) (a=b=5.1 Å). These oxide films were grown at a substrate temperature of 500 K, O₂ background of 10⁻⁶ Torr, and growth rate of ~10 Å/min, followed by annealing in O₂ (10⁻⁶ Torr, 1000 K) and further Ti deposition and annealing in O₂. Subsequent deposition of Cr under UHV at room temperature results in a strained epitaxial Cr₂O₃(0001) monolayer with magnetic ordering and exchange bias from 280 K to at least 315 K.

Titania film growth on Al₂O₃(0001) is characterized by LEED data (Fig. 1) and XPS data (Fig. 2). LEED data demonstrate the initial formation of a (111)-oriented oxide film (Fig. 1b) with an estimated thickness (based on measured growth rate) of 49 Å. Significant concentrations of Ti(IV) and Ti(III) are observed by XPS (Fig. 2a), resulting in an estimated oxide stoichiometry of ~ TiO_{1.7}, and a Ti₂O₃-characteristic lattice constant of 5.1 Å. Corresponding EELS spectra (not shown) indicate a band gap near 3 eV, characteristic of rutile TiO₂ [5] but also with a sloping feature at loss energies < 1 eV (Fig. 3a) consistent with electrons in mid-gap states, or of the band gap in corundum-phase Ti₂O₃ [6]. The LEED, XPS and EELS data are therefore indicative of oxygen-rich Ti₂O₃(111) or an oxygen-poor phase of TiO₂(111) with the lattice constant characteristic of Ti₂O₃(111). We refer to such films as TiO_{1.7}(111) films.

Annealing of TiO_{1.7}(111) in 10⁻⁶ Torr O₂ at 1000 K results in the maintenance of the hexagonal LEED pattern (Fig. 1c), although substantial charging is observed, with the electron beam migrating off of some samples or inducing significant blurring of the hexagonal LEED pattern (as in Fig. 1c,d) in others. This annealing also drastically decreased or effectively eliminated the Ti(III) feature in the XPS (Fig. 2b). EELS spectra also showed the elimination of the sloped feature at loss energies < 1 eV, indicating the elimination of mid gap O vacancy states and consistent with the observed increased sample charging during LEED or XPS. That such films retained the previous lattice structure, however, is evidenced by the somewhat faint hexagonal LEED pattern (Fig. 1c) and the fact that subsequent Ti deposition under the same conditions as those described above would immediately produce LEED and XPS spectra as in Fig. 1b, Fig. 2a, and corresponding changes in EELS spectra. The data therefore indicate that annealing of TiO_{1.7}(111) in O₂ produces stoichiometric TiO₂, but with (111) orientation and a lattice constant remaining at 5.1 Å. We refer to such films as corundum-phase TiO₂(111) (c-TiO₂(111)). These results are similar to those recently reported for XPS analyses of the surfaces of Ti₂O₃ single crystals prepared by cutting in ambient prior to insertion into vacuum [7].

Deposition of ~ 4.4 Å Cr at room temperature on c-TiO₂(111) yields the formation of additional O vacancies in the Ti 2p XPS and formation of Cr(III), while retaining the overall hexagonal LEED pattern (albeit faint) previously observed (Fig. 1c,d). Ex-situ planar MOKE data (Fig. 3) indicate chromia magnetic ordering hysteresis at 300 K (T_N = 307 K), but with significant exchange bias, consistent with chromia boundary layer magnetization interaction with O-related defect spins in the titania substrate. The observed hysteresis in planar MOKE indicates canting of the chromia magnetization away from the thin film normal. The observation of magnetic ordering at 315 K, above the chromia T_N of 307 K, is also characteristic of strain induced in the chromia lattice, induced either by possible O vacancies in chromia, or to adoption of the substrate lattice constant of 5.1 Å, larger than that of bulk chromia (4.9 Å) [8].

The data reported here show that hexagonally-oriented titania films with a stoichiometry of ~ TiO_{1.7} but with the lattice spacing of Ti₂O₃ can be grown by MBE on Al₂O₃(0001). Subsequent annealing in O₂ yields films with the stoichiometry of TiO₂ but with the lattice spacing of Ti₂O₃; c-TiO₂(111). Such films support the subsequent MBE growth of epitaxial chromia films, exhibiting consistent magnetic behavior between 280 K at 315 K. These results therefore show that careful control of deposition conditions can yield novel oxide nanostructures with interesting potential applications in spintronics and other areas.

References

Supporting Data

- [1] J. Qiu, G. Zeng, et al. Microscopic study of atomic layer deposition of TiO₂ on GaAs and its photocatalytic application. *Chemistry of Materials*. 27 (2015) 7977-7981.
- [2] K. Vasu, et al.. Atomic layer deposition of p-type epitaxial thin films of undoped and N-doped anatase TiO₂. *ACS Appl Mater Interfaces*. 8 (2016) 7897-7901.
- [3] P. Han, et al. Outstanding memory characteristics with atomic layer deposited Ta₂O₅/Al₂O₃/TiO₂/Al₂O₃/Ta₂O₅ nanocomposite structures as the charge trapping layer. *Appl Surf Sci*. 467-468 (2019) 423-427.
- [4] T. Sarkar, et al. Electron transport at the TiO₂ surfaces of rutile, anatase and strontium titanate: The influence of orbital corrugation. *ACS Appl Mater Interfaces*. 7 (2015) 24616-24621.
- [5] M.R. Bayati, et al. Domain epitaxy in TiO₂/α-Al₂O₃ thin film heterostructures with Ti₂O₃ transient layer. *Appl Phys Lett*. 100 (2012) 251606.
- [6] Y. Li, et al., Orthorhombic Ti₂O₃: A polymorph-dependent narrow-bandgap ferromagnetic oxide. *Adv Funct Mater*. 28 (2018) 1705657.
- [7] S. A. Chambers, et al., X-ray photoelectron spectra for single crystal Ti₂O₃: Experiment and theory, *Phys Rev B*. 96 (2017) 205143
- [9] Iori Tanabe, et al. Strain induced super-paramagnetism in Cr₂O₃ in the ultra thin film limit, *Mat Res Soc Symp. Proc.* 1729 (2015) DOI: 10.1557/opl.2015.5

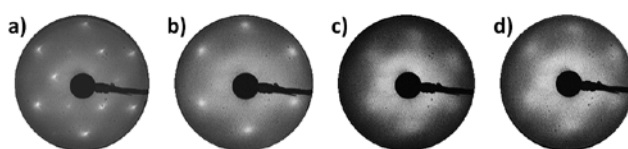


Fig. 1 LEED images of (a) a clean Al₂O₃ (0001) substrate; (b) a 49 Å thick TiO_{1.7}(111) film deposited on Al₂O₃(0001); (c) a similar film as in (b) but annealed at 1000 K in 10⁻⁶ Torr O₂ to yield a near-stoichiometric TiO₂; (d) after deposition of ~ 1 ML of Cr₂O₃. The images were taken at 60 eV (a,b), 100 eV (c) and 80 eV (d). Images of films with stoichiometric TiO₂ (c,d) were strongly affected by sample charging.

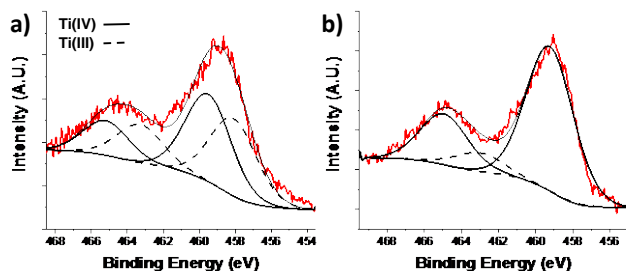


Fig. 2. Ti 2p XPS data deconvoluted to show relative concentrations of Ti(IV) and Ti(III) cations: (a) TiO_{1.7} (111) film ~ 50 Å thick; (b) TiO₂(111) film produced by annealing (a) in O₂; The spectra are deconvoluted into Ti(IV) and Ti(III) components (solid and dashed traces, respectively).

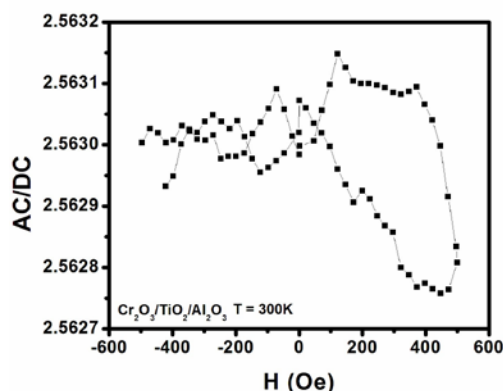


Fig. 3 Planar MOKE Data for ~ 1 ML Cr₂O₃/TiO₂(111) acquired at (left) 300 K. Similar behavior is observed from 280 K up to at least 315 K.