BNL-114234-2017-JA

Enhanced Magnetization of Cobalt Defect Clusters Embedded in $\text{TiO}_2\text{-}\delta$ Films

D. L. Cortie, D. J. Sprouster

Submitted to the Journal Applied Materials & Interfaces

August 23, 2017

Nuclear Sciences & Technology Department

Brookhaven National Laboratory

**U.S. Department of Energy
USDOE Office of Science (SC),
Nuclear Physics (NP) (SC-26)**

Notice: This manuscript has been authored by employees of Brookhaven Science Associates, LLC under Contract No. DE-SC0012704 with the U.S. Department of Energy. The publisher by accepting the manuscript for publication acknowledges that the United States Government retains a non-exclusive, paid-up, irrevocable, world-wide license to publish or reproduce the published form of this manuscript, or allow others to do so, for United States Government purposes.

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or any third party's use or the results of such use of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof or its contractors or subcontractors. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

Enhanced Magnetization of Cobalt Defect Clusters Embedded in $\text{TiO}_{2-\delta}$ Films

David L. Cortie,^{*,†,‡,§,¶} Yury Khaydukov,^{||,⊥} Thomas Keller,^{||,⊥} David J. Sprouster,^{#,▽} Jacob S. Hughes,[▽] James P. Sullivan,^{▽,Ⓢ} Xiaolin L. Wang,[‡] Anton. P. Le Brun,[§] Joel Bertinshaw,^{§,Ⓢ} Sara J. Callori,^{§,Ⓢ,◆} Robert Aughterson,[§] Michael James,[§] Peter J. Evans,[§] Gerry Triani,[§] and Frank Klose^{§,¶}

[†]Research School of Chemistry, Australian National University, Canberra, Australian Capital Territory 2601, Australia

[‡]The Institute for Superconducting and Electronic Materials, University of Wollongong, Wollongong, New South Wales 2522, Australia

[§]Australian Nuclear Science and Technology Organization, Lucas Heights, New South Wales 2234, Australia

^{||}Max Planck Institute für Festkörperforschung, Stuttgart 70569, Germany

[⊥]Max Planck Society, Outstation at the MLZ, Garching 85748, Germany

[#]Brookhaven National Laboratory, Upton, New York 11973, United States

[▽]ARC Centre for Antimatter–Matter Studies, Australian National University, Canberra Australian Capital Territory 0200, Australia

[Ⓢ]School of Physics, University of New South Wales, Sydney, New South Wales 2052, Australia

[◆]Department of Physics, California State University, San Bernardino, California 92407, United States

[¶]Department of Physics and Materials Science, City University of Hong Kong, Kowloon, Hong Kong Special Administrative Region, China

Supporting Information

ABSTRACT: High magnetizations are desirable for spintronic devices that operate by manipulating electronic states using built-in magnetic fields. However, the magnetic moment in promising dilute magnetic oxide nanocomposites is very low, typically corresponding to only fractions of a Bohr magneton for each dopant atom. In this study, we report a large magnetization formed by ion implantation of Co into amorphous $\text{TiO}_{2-\delta}$ films, producing an inhomogeneous magnetic moment, with certain regions producing over $2.5 \mu_B$ per Co, depending on the local dopant concentration. Polarized neutron reflectometry was used to depth-profile the magnetization in the Co: $\text{TiO}_{2-\delta}$ nanocomposites, thus confirming the pivotal role of the cobalt dopant profile inside the titania layer. X-ray photoemission spectra demonstrate the dominant electronic state of the implanted species is Co^0 , with a minor fraction of Co^{2+} . The detected magnetizations have seldom been reported before and lie near the upper limit set by Hund's rules for Co^0 , which is unusual because the transition metal's magnetic moment is usually reduced in a symmetric 3D crystal-field environment. Low-energy positron annihilation lifetime spectroscopy indicates that defect structures within the titania layer are strongly modified by the implanted Co. We propose that a clustering motif is promoted by the affinity of the positively charged implanted species to occupy microvoids native to the amorphous host. This provides a seed for subsequent doping and nucleation of nanoclusters within an unusual local environment.

KEYWORDS: nanoclusters, nanomagnetism, spintronics, dilute magnetic oxide semiconductor, nanocomposite

INTRODUCTION

The miniaturization of semiconductor elements has been the central impetus in the field of nanoelectronics; however, modern technology is approaching intrinsic limitations as the device dimensions converge toward the single-nanometer scale. At this point, issues with heat dissipation and quantum uncertainties make traditional transistor designs unreliable.¹ One route to circumvent this issue is to incorporate

multifunctional nanomaterials that achieve more operational power in equivalent space by exploiting the interplay of semiconducting and magnetic properties.² To this end, Co: $\text{TiO}_{2-\delta}$ composite materials are very promising because

Received: November 24, 2016

Accepted: February 23, 2017

Published: February 23, 2017

Figure 1. (a) The 68 nm thick amorphous TiO_2 thin films were synthesized with atomic layer deposition before (b) Co was implanted at low energies (20–60 keV). (c) The resulting nanostructures were studied with low-angle polarized neutron scattering with specular reflected beams.

Figure 2. (a) A large magnetic moment is measured at 300 K and at 10 K in a $(\text{Co,Ti})\text{O}_{2-\delta}$ film implanted with an average of 10 atomic percent (%) Co, corrected for the diamagnetic signal of the Si substrate. The right-hand axis is the equivalent volume magnetization assuming uniform magnetization over the 26 nm doped sublayer. (b) The intensity of low-angle reflected spin-polarized neutrons (spin up R^+ , red, and spin down R^- , blue symbols) from the 10% sample shows a large spin asymmetry caused by the magnetization in the thin film layer. The solid lines are calculated reflectivity signals derived from the refined real-space chemical and magnetic model depth profile shown in Figure 4e,f.

they show the coexistence of tunable conductivity and magnetic properties at room temperature in several nanomorphologies including thin films,^{2–4} particles,^{5,6} and rods.⁶ The two most common TiO_2 polymorphs, anatase and rutile, have both been labeled “dilute magnetic oxide semiconductors” (DMOS) and are widely reported to support magnetism associated with the intrinsic effect of Co substitution onto the titanium site.^{2,7–9} Segregation of metallic Co nanoclusters is also common^{8,10} and can undoubtedly contribute to the magnetic signal. The microstructural details have an important influence on the resulting magnetic moment. The electronic structure of the cobalt depends closely on its bonding environment, and in particular, the number of unpaired 3d electrons. A cluster, by definition, consists of two or more cobalt atoms in a nearest-neighbor or next-nearest-neighbor configuration. In contrast, from the microstructural point of view, “matrix-isolated” cobalt species are those surrounded by titanium and oxygen neighbors and well-separated from other cobalt atoms. Thus, for example, metallic clusters which are dominated by Co–Co bonding should result in Co^0 state and possess a different magnetic moment compared to matrix-isolated cobalt, which are typically coordinated by O^{2-} to form a Co^{2+} state. Importantly, Co-rich TiO_2 materials produce a strong Anomalous Hall Effect both with^{4,11} or without⁸ observable metallic clustering, providing a viable mechanism to control device resistance based on local

magnetic fields. Indeed, these favorable properties have led to the material’s inclusion in prototype electric field effect^{7,12} and spin injection devices.¹³ Unfortunately, the observable magnetic moment typically varies between 0.01 and 1.5 Bohr magneton (μ_B) per Co atom in $\text{TiO}_{2-\delta}$, depending on the synthesis route, although occasionally larger values in the range 2–2.5 μ_B have been reported.^{9,14} The wide range of values indicates that the local chemistry and coordination of the Co is poorly controlled, showing an erratic dependency on stoichiometry and disorder. This has hindered the uptake of $\text{Co}:\text{TiO}_{2-\delta}$ because reliable device applications require a reproducible and large magnetic moment in order to have predictable effects on electron transport. While it is universally agreed that the magnetic properties are closely linked to details of the local structure surrounding the Co, including the ubiquitous role of nano-cluster formation, it is largely unknown which synthesis methods can be used to generate larger magnetizations and control cluster formation.

In this work, we reveal that ion-beam synthesis of Co implanted into amorphous $\text{TiO}_{2-\delta}$ films leads to the self-assembly of ultrasmall embedded magnetic defect clusters with magnetizations that are significantly higher than the majority of reports for similar $\text{Co}:\text{TiO}_{2-\delta}$ systems. It is quite well-known that ion implantation at high doses leads to the formation of embedded magnetic nanocrystals in SiO_2 ^{15,16} and TiO_2 ^{11,16–18}

with small sizes that depend on the implanted concentration¹⁶ and ion beam damage.^{1,5,19} However, it is unclear how the local magnetic properties vary across the beam-stopping profile, particularly at lower doses. We show that the local magnetic moment introduced per implanted impurity can even approach the upper limits set by Hund's rules for a Co atom, a remarkable and useful result. Depth profiling with polarized neutrons reflectometry (PNR) provides compelling evidence that the high magnetization is directly correlated with the Co local structure.

■ RESULTS AND DISCUSSION

To synthesize the Co:TiO_{2-δ} nanolayers, we used atomic layer deposition (ALD) to deposit amorphous TiO₂ films on (100)-oriented Si substrates passivated by the native SiO₂ layer (thickness ~2 nm). The starting thickness of the titania layers was selected between 68 and 70 nm to completely isolate the implanted cobalt layer within the titania layer. Ion implantation of Co was then performed at beam energies of 20–60 keV. This two-step synthesis process is illustrated schematically in Figure 1a,b. At the second step, a range of ion beam doses between 0 and 2.0×10^{16} ions per cm² were used to modify the starting TiO₂ films, and magnetic characterization was performed in a Quantum Design PPMS. Ion doses of 2.0×10^{16} ions per cm² produced nanocomposite films with a large volume-average magnetization and low remanence, Figure 2a. At this level of ion concentration, elemental profiling shows that the atomic percentage of Co lies in a gradient between 10 and 16% in the implanted layer. Similar magnetic properties to those in Figure 2 have now been reported for Co-rich TiO₂ synthesized by a range of methods,^{4,6,9,10,20,21} however, upon close inspection, the saturation moment shows a puzzling degree of variability. The low coercive field ($H_c < 200$ Oe), on the other hand, is fairly reproducible across the dilute magnetic oxide family and has been attributed to either superparamagnetic behavior⁴ or an intrinsic dilute magnetic ground state complicated by a wandering anisotropy axis.²² While the magnetometry clearly shows the presence of a ferromagnetic component, the raw data in volume-averaged techniques can hide considerable nanoscale complexity within a single number, the net magnetic moment. This is usually divided by the assumed magnetic volume or known molar concentrations to produce units of emu/cm³ or μ_B per species. For example, in TiO₂ doped with magnetic 3d ions, it is typical to assume that the net moment originates entirely from the dopant ions, all of which make identical magnetic contributions. Adopting this viewpoint can be highly misleading in complex nanomagnets where variation in the local chemical environment will naturally produce a variation in the local magnetization. Thus, while the “apparent” moment per Co is a useful figure-of-merit, physically the correct picture entails magnetic inhomogeneity due to the stochastic placement of point defects in the DMOS family. For instance, in low dose regions, it is probable that matrix-isolated cobalt defects are formed although these typically only show weak paramagnetic properties.¹⁷ To resolve these issues, we used a powerful method known as polarized neutron reflectometry (PNR) which works by analyzing the reflection of cold neutrons at low scattering angles ($<5^\circ$) from a planar system. This scattering technique can detect both the isotopic composition and the magnetization in a thin film. As a probe, PNR has an inherent sample-depth resolution making it trivial to “filter out” surface impurity or substrate contributions to the magnetism. Moreover, the technique measures the nanometer-

scale magnetization per volume in absolute units owing to the intrinsic dipole moment of the neutron.²³ This permits straightforward quantitative interpretation which is particularly advantageous for materials like Co:TiO_{2-δ}, where the intricate local electronic structure complicates quantitative interpretations of X-ray circular dichroism spectra based on the sum-rules.²⁴

The neutron reflectometry patterns on the 10% Co:TiO_{2-δ} film (Figure 2b) clearly show a large magnetization that originates from the thin implanted layer. This is evident as a clear difference between the spin-up (R^+) and spin-down (R^-) reflection pattern. To measure the two reflectivity signals, the incoming neutron polarization is defined using a presample polarizing supermirror and spin-flipper, and the outgoing reflected beam is measured on an area detector.²⁵ To facilitate comparison between different operating wavelengths, the reflection pattern is plotted as a function of the universal scattering vector, $Q_z = 4\pi \sin \theta / \lambda$, where θ is the scattering angle defined in standard Bragg–Brentano geometry.²⁵ The distinct Q_z -dependence of the reflection patterns for the two neutron spin states, as shown in Figure 2b, encodes depth-dependent information regarding the interfering waves reflected from various interfaces. It is quite unambiguous that the magnetic signal originates from the Co:TiO_{2-δ} film because this alone explains the Q_z dependency. For example, a semi-infinite magnetic substrate would produce reflection patterns which fall off according to Fresnel's law giving an intensity proportional to Q_z^{-4} above the angle of critical external reflection, with a constant difference between the spin up and spin down channels. In contrast, the experimental reflectivity data shows clear maxima with oscillating intensity (Kiessig fringes) caused by the finite thickness of the film. Likewise, the reflected signal for each spin state shows a complex, nonmonotonic dependency on Q_z . Before we discuss a detailed scattering-model, which numerically describes the distributed real-space source of the magnetism, it useful to extract the basic magnetic features in a model-free way by calculating the neutron spin asymmetry (SA):

$$SA(Q) = \frac{R_+ - R_-}{R_+ + R_-} \quad (1)$$

Unlike the total reflectometry patterns, the spin asymmetry is purely related to the local magnetic moment in the sample, and so it is useful as the first step to characterize magnetic properties directly.

The strong neutron spin asymmetry from the 10% implanted Co:TiO_{2-δ} (Figure 3) indicates a large internal magnetic moment throughout the temperature range 5–300 K. The observed peak SA occurs at $Q_z = 0.12 \text{ nm}^{-1}$ and exceeds 60% (Figure 3a), which is large compared to the spin asymmetries typical in dilute magnetic systems²⁶ and rivals that of standard magnetic alloys.^{27,28} Interestingly, the spin asymmetry (and therefore the magnetic moment of the sample) continues to increase with the applied external field up to the maximum experimental field of 1 T (Figure 3b). This is quite different from standard superparamagnetic behavior and reminiscent of the high anisotropy magnitude noted in very small clusters of Co in 2D environments.²⁹ The nonsaturating high field property has not been noted in past work for Co embedded in a three-dimensional TiO₂ host matrix. It is, however, quite difficult to detect using “macroscopic” magnetometry like the VSM or SQUID techniques (Figure 2a) because the overall

Figure 3. (a) The neutron spin asymmetry has a strong Q_z dependency and a weak temperature dependency under applied fields of 1 T, where the magnitude and the Q_z dependence can be fitted to the chemical and magnetic model described later in the text. (b) The field-dependence of the peak spin asymmetry does not saturate at 1 T. Lines are guides to the eye. (c) The peak neutron spin asymmetry shows very little temperature dependence between the 300–5 K, ruling out a strong paramagnetic contribution. Lines are guides to the eye.

high-field signal includes the role of the substrate, which produces a dominant diamagnetic contribution due to its relatively high volume. If the film itself shows a small linear response in the high field regions, this is convoluted with an overwhelming diamagnetic signal and it is challenging to reliably subtract the latter contribution in order to measure the intrinsic behavior of the nanolayer. In contrast, PNR is unaffected by complications of diamagnetic or weak paramagnetic responses because these produce very low magnetizations per volume. Instead, the PNR signal is dominated by scattering effects from large local net magnetization, typically caused by a well-aligned collinear spin structure from ferromagnetic states. Consequently, the small value of the neutron spin asymmetry at low fields (Figure 3b) confirms the trait noted in the hysteresis from the VSM data (Figure 2a). This shows that, without sufficient applied field, the magnetic moments in the composite do not stay well aligned in any specific direction. The first possible reason for this is there are inhomogeneous magnetically ordered patches in the nanocomposite layer that experience a distribution of local spin anisotropies and consequently have a distribution of magnetization angles that are only coaligned in a magnetic field and relax under zero field. The second possible explanation would be the existence of purely paramagnetic spin behavior. It is

simple to directly rule out the second scenario because the magnetic moment in the Co:TiO_{2-δ} nanocomposite only changes moderately with temperature (Figure 3c), which indicates a strong form of magnetic exchange coupling is present. As the neutron spin asymmetry is a very reliable method to study the intrinsic nanomagnetic features, it provides direct evidence that these magnetic properties originate from the composite thin film region and the substrate and surface play no detectable role. The unusual combination of properties immediately shows that the magnetic state in the sample is more interesting than a thermally governed paramagnetic response expected for uncoupled cobalt atoms. To further investigate the quantum chemical reasons behind the magnetic coupling, we determined precise values for the local magnetization and chemical-isotope composition by analyzing the neutron data quantitatively.

To fit the neutron reflectometry patterns, we used a robust multitechnique-based method, and this provides unambiguous evidence of anomalously strong impurity magnetic moments in the implanted layer. Refinement of neutron reflectometry data using complementary information from transmission electron microscopy (TEM) and X-ray reflectometry (XRR) is an increasingly popular way to construct an accurate description of the local atomic and magnetic concentrations in a thin film or at an interface. Formally, the neutron scatters due to a depth-dependent quantum potential comprised of a nuclear (isotope) scattering (ρ_n) and magnetic (ρ_m) scattering length density (SLD)²³

$$V_{\pm} = \frac{2\pi\hbar^2}{m_n}(\rho_n \pm \rho_m) \quad (2)$$

where m_n is the neutron mass. The two components can be calculated by summing over J isotopes each having concentration N_i , coherent scattering length (b_i), and magnetic moment μ_i :

$$\rho_n = \sum_{i=0}^{i=J} N_i b_i \quad (3)$$

$$\rho_m = C \sum_{i=0}^{i=J} N_i \mu_i \quad (4)$$

where the continuum description is valid for the low-angle scattering, and C is a constant relating the strength of the magnetic scattering to the number density of Bohr magnetons ($C = 2.645 \times 10^{-5} \mu B^{-1}$). Because the values of the neutron optical constants b_i are well-known, the first term ρ_n can be independently determined if the local chemical concentrations (N_{Ti} , N_{Co} , N_O) are measured using standard probes such as TEM, X-ray photoemission spectroscopy (XPS), and XRR. In this work, we used several independent methods to determine the chemical concentrations, with particular emphasis on the absolute value of cobalt concentration. First, the relative concentration of the elements was determined from XPS peak-fitting after using argon-beam etching and calibrating the relationship between etch rate and depth scale using the total thickness of the Ti layer. To confirm the depth scale calibration, qualitative confirmation of the cobalt and titanium profile was provided using EDS mapping in the cross-sectional TEM. Independent determination of the cobalt profile was also provided by secondary mass ion spectroscopy (SIMS). For the purposes of fitting the reflectometry, the absolute concen-

Figure 4. (a) High resolution TEM shows inhomogeneous clustering at depths of ~ 20 nm. (b) The Co distribution detected by EDS at the buried implant region. (c) The Monte Carlo simulations of the stopping profile of the Co agree quite well with the depth-resolved XPS described later in the text. (d) The five-layer scattering model constructed to fit the neutron data (e) The results of the fitted real-space scattering length density model. (f) The magnetization determined from the scattering length density model.

trations, rather than the relative percentages, need to be known, and this was achieved by constraining the relative concentrations to the XPS result and then scaling N , the total atomic density, when fitting the X-ray reflectometry where it is the only free parameter. The obtained N was then adopted in the neutron fits. As a separate independent measure of the absolute cobalt and titanium concentrations, Rutherford backscattering (RBS) was conducted on the heaviest-doped sample. The various methods agreed well within a few atomic percent. In particular, the cobalt concentration was known to within 1 atomic % in the region of interest. Having constructed a robust chemical profile of the sample, the neutron data could be fitted simply by adjusting the only free parameter, namely the magnetic part (ρ_m) of the scattering length density as a function of depth.

To summarize the steps used in fitting the reflectometry data, Figure 4a shows the high-resolution transmission electron microscopy cross-section of the amorphous TiO_{2-x} film implanted with mean Co concentration of $\sim 10\%$. The elemental map from energy-dispersive spectroscopy (EDS) of the Co signal (blue) is overlaid on the O signal (white) qualitatively showing the presence of Co buried beneath the surface (Figure 4b). The Monte Carlo simulations of the ion profile were generated using the SRIM software,³⁰ and the theoretical Co profile is very close to the experimental measurements (Figure 4c). Using the reflectometry fitting routines in MOTOFIT³¹ and SIMULREFLEC,³² the X-ray and neutron reflectometry data were fitted to a five-layer model (Figure 4d) with the relevant layer thicknesses and interface-mixing parameters designed to reproduce the chemical profile of the implanted TiO_2 . The latter resembles a 1D Gaussian function for the implant region superimposed on a step function of the unperturbed regions of the TiO_2 layer, as reflected in the nuclear scattering profile (Figure 4e). Thus, the main adjustable parameter in the neutron model was the local magnetization within each sublayer, and other parameters were constrained within ($\pm 2\%$). Refining the quantity ρ_m leads to the scattering length density model presented in Figure 4e, where the neutron spin up and spin down scattering length densities (SLD) are defined as $\text{SLD}(\pm) = \rho_n(\pm) + \rho_m$. The calculated reflectometry from this real-space profile produces excellent fits to the experimental scattering data (solid lines in Figure 2b and Figure 3a), thereby showing that the magnetic component ρ_m makes a significant contribution in the

implanted layer. As the neutron scatters off the total magnetization, expressed as the sum over all present isotopes, it is not element-specific and thus we can freely rewrite eq 4 as the depth-dependent net magnetization in emu/cm^3 :

$$\rho_m = C'm \quad (5)$$

with $C' = 2.853 \times 10^{-9} \text{ \AA}^{-2} \text{ cm}^3/\text{emu}$ and the magnetization m in emu/cm^3 . The magnetization determined via ρ_m is very large across most of the ion beam layer (Figure 4f) with values in the range $100\text{--}250 \text{ emu}/\text{cm}^3$. The temperature variation is relatively weak so that the 10 K data captures the main features. There are several other interesting features revealed in the details of the magnetic depth profile, as we discuss below.

The magnetic depth profile shows negligible magnetization ($\rho_m \rightarrow 0$) in the surface, nonimplanted, and substrate regions at all temperatures. This unambiguously establishes that Co-free regions of the $\text{TiO}_{2-x}/\text{SiO}_2/\text{Si}$ structure do not contribute a detectable magnetic moment. This stands in contrast to past magnetometry studies that have reported lattice defects, surfaces, and oxygen vacancies,^{5,33} such as those caused by ion beam damage,³⁴ are capable of producing a significant magnetic moment in defective TiO_2 , even in the absence of a magnetic impurity (Co). Collectively, these forms of “defect-induced” magnetism belong to the so-called d^0 paradigm³⁵ and have become the subject of much intensive research and speculation. Nonetheless, if any form of strong d^0 magnetism was present in the samples, we would detect an extremely different Q_z dependence in the neutron spin asymmetry.

A second interesting feature in the magnetic depth profile is the quantitative size of the magnetic moment introduced per cobalt. On the basis of the latter discussion, our data establishes that, if lattice defects do contribute significantly to the magnetization, then this only occurs via cooperation involving nearby Co necessary to “trigger” the magnetic state (i.e., by spin-polarizing the defect structure around the cobalt). Under these conditions, it is reasonable to equate the observed magnetization with the moment introduced per Co atom in order to calculate the standard figure-of-merit and compare with past work. However, we stress that this should not be interpreted as the actual “magnetic moment localized on each cobalt dopant” because the magnetization does not originate only from the cobalt but also involves spin density that is likely to be delocalized across the entire defect structure surrounding the cobalt including neighboring Ti, O, and vacancy regions.

Nevertheless, to calculate the moment triggered by each Co atom's defect structure, we simply divide the depth-dependent magnetization (m) from the neutron ρ_m by the depth-dependent value of the Co concentration (N_{Co}) measured by XPS and XRR. This is equivalent to setting $\mu_{\text{Ti}} = \mu_{\text{O}} \sim 0$ in eq 4 and then evaluating the moment assuming that it is only associated with the Co species (μ_{Co}). Remarkably, we find that the apparent moment introduced per Co (μ_{Co}) is above $2.0 \mu_{\text{B}}$ in approximately half of the implanted layer and in certain regions gives local magnetic moments as high as $2.7 \pm 0.3 \mu_{\text{B}}$ per Co atom. The sources of uncertainty in the result arise from the accuracy in measured Ti:Co chemical profile, and the neutron fitting uncertainty for the magnetic moment that was assessed using a previously reported method.³⁶ This large moment appears to be significant because the magnetic moment introduced by Co^{2+} in substitutional sites in TiO_2 has been reported to range between 0.01 and $2.2 \mu_{\text{B}}$ per cobalt,¹⁴ although the best consensus available gives values in the range $1.1\text{--}1.4 \mu_{\text{B}}$ per cobalt.¹⁰ Metallic segregation is not a straightforward explanation for the enhanced magnetic moments because bulk metallic Co only gives a magnetic moment of $1.72 \mu_{\text{B}}$ per Co atom in the standard metallic phases, and likewise, standard-sized nanocrystals (5–20 nm) provide moments of $1.7 \mu_{\text{B}}$ per Co.³⁷ This indicates a second mechanism is present to explain the enhanced magnetization. It has been shown that ultrasmall isolated nanoclusters of metallic Co^0 with less than 10–20 atoms provide a magnetic moment between $2.5\text{--}3.5 \mu_{\text{B}}$ per cobalt for free-standing clusters,³⁸ or $2.1\text{--}2.4 \mu_{\text{B}}$ near a surface.²⁹ Such moments, which are contingent on finite size and surface area ratios, occur for nanoclusters with volumes less than 1 nm^3 in size and are aggressively reduced as additional atoms are added, primarily through loss of the angular momentum component.^{29,38} To date, the smallest embedded Co nanocluster directly observed in an oxide host were formed using implantation, giving diameters reported as $1.5 \pm 1 \text{ nm}$.¹⁶ However, there is to date no indication that enhanced moments will survive if such a particle is embedded in a crystalline or amorphous 3D host. In the crystalline anatase, for example, past DFT calculations for four-atom cobalt clusters embedded in the ordered lattice found only a net $0.93 \mu_{\text{B}}$ per cobalt.³⁹ It is thus equally likely that an alternate type of defect cluster is present, possibly involving matrix-isolated Co species in a local environment that is atypical for a crystalline TiO_2 matrix but results in an enhanced moment in the amorphous TiO_2 structure. For example, recent DFT calculations on cobalt in TiO_2 anatase show that the $(\text{Co}_{\text{Ti}}\text{V}_{\text{O}})^{1+}$ defect has a total magnetic moment of $1.9 \mu_{\text{B}}$, with about $1.5 \mu_{\text{B}}$ coming from cobalt and the rest from the defect surrounding complex. The per site magnetic moment of Co^{2+} state in bulk and nanoparticle CoO is even higher, producing $3\text{--}4 \mu_{\text{B}}$,⁴⁰ reflecting the different coordination of the Co. Thus, it seems that the numerically large magnetic moments in our sample are a signature of a novel local environment surrounding the implanted species, however, to understand the mechanism it is important to identify whether metallic (Co^0) or oxidized (Co^{2+}) state plays the dominant role.

X-ray photoemission spectra of the 10% implanted $\text{Co}:\text{TiO}_{2-\delta}$ show the characteristic peaks attributed to a mixture of the Co^{2+} and Co^0 valence state (Figure 5a), however, the dominant state is Co^0 through the majority of the sample and this is largely independent of ion beam treatment times (Figure 5b). Peak-fitting analysis of the Co 2p peak in Figure 5a

Figure 5. (a) Evolution of the Co edge XPS peak after various ion-beam etching times, revealing the subsurface cobalt layer. The Co^0 feature (BE = 780 eV) dominates the signal at the peak implant region, whereas some contributions from Co^{2+} can be observed in shoulder features at shallower depths. (b) An enlarged region of the near-surface depths illustrates that the Co^{2+} features, including the shake up satellites, are strongly suppressed at a short distance beneath the surface, and the Co^0 feature dominates for the majority of the sample. (c) The atomic percentages determined from XPS peak fitting and integration, as a function of etch time calibrated to depth using the EDS and XRR data.

demonstrates that the majority (80% or more) of the integrated signal is located at the peak with binding energy of 778.3 eV for the Co $p^{3/2}$ line, with the spin orbit splitting expected for Co metal ($\Delta = 15.0 \text{ eV}$). The primary peak matches the typical value for Co^0 metal state (778.2 eV) and quite different from the 2^+ oxide (779.7 eV). This is highly consistent with past X-ray absorption spectroscopy that also reports that the Co^0 state is dominant in TiO_2 after ion beam implantation and inferred that this showed the presence of metallic Co nanoclusters.¹⁸ Moreover, where present, the Co^{2+} state produces a distinctive set of shakeup satellite peaks, unlike that of Co^0 , and in our case, these are only observable near the surface of the sample. To search for depth-dependent variation across the implant

Figure 6. X-ray reflectometry and neutron reflectometry for the four samples with varying degrees of ion beam implantation corresponding to (a) 0% cobalt, (b) 4% cobalt, (c) 6% cobalt, and (d) 10% cobalt. All samples were measured under 0.3 T at 300 K. The two more heavily doped samples show a clearly observable spin asymmetry.

layer, an argon ion beam was used to etch the sample to reveal the buried layers, and the etch rate was calibrated by comparing the profile with the TEM, EDS, and XRR profiles. Figure 5b shows that the weak satellite Co^{2+} features are observable at very shallow depths (<3 nm), consistent with surface oxidation playing a role, however, the single metallic Co^0 peak becomes dominant deeper into the TiO_2 . Figure 5c shows the atomic percentages of the various elements in the sample measured by XPS peak fitting and integrating the elemental peaks. Notably, the Co^{2+} surface regions do not produce large magnetic moments according to the real-space picture from the neutron scattering, and this is consistent with an antiferromagnetic exchange typical for Co oxide phases. Moreover, given the low relative fraction deeper into the sample, it is unlikely that the Co^{2+} species can be responsible for the large net magnetic moments observed there. The peak Co concentration occurs at a depth of 18–24 nm, which is also where the fraction of $\text{Co}^0/\text{Co}^{2+}$ in the XPS is at its maximum. Close inspection of the enlarged high resolution TEM image at these depths (Supporting Information), and the related energy-filtered maps, do show some increased inhomogeneity in this regions, with many smaller features and some of the larger irregularly shaped features having a length scale between 1 and 4 nm. Notably, in our case, the contrast presumably is partly derived from strain fields around the cobalt and do not necessarily

reflect the particle size. Such features are only detectable in the cross-sectional TEM beneath the surface at the peak of the implantation dose. The latter picture is corroborated by the EDX mapping, which shows nonuniformity in the cobalt map. Consistent with the metallic volume fraction, the nuclear SLD ρ_n needed to accurately describe the neutron patterns is *lower in the implanted region*. Thus, the comparably noninvasive technique also indicates a sizable fraction of missing oxygen consistent with an increased metallic volume fraction. On the basis of these results, it is logical that a large portion of the magnetic signal originates from small Co^0 metallic clusters. On the other hand, the colossal magnetization indicates that the details of the orbital and electronic magnetic polarization around the Co^0 are quite different from the standard metallic state. This warrants further attention as it reflects certain unique properties of the embedded ultrasmall structures in the amorphous host tied to the specific local structure generated in the ion implantation method.

The formation of metallic nanoclusters via ion-beam synthesis is generally expected under sufficiently high doses in the as-implanted state, and this process is theoretically capable of growing extremely small nanoclusters compared to conventional routes.¹⁹ While the typical method to form nanoclusters via ion-beam synthesis relies on high temperature annealing, in our work no annealing was performed. The

growth resulting from the spontaneous assembly of clusters in the ion beam implantation process is thus very distinct from conventional nanoparticle formation. For instance, high temperature annealing in an ambient atmosphere often results in the oxidation and diffusion of cobalt species toward a surface or interface in TiO_2 ,^{4,11} followed by particle growth proceeding by Ostwald ripening whereby particles amalgamate to form larger entities. In contrast, the majority of the cobalt appears in regions with no obvious microstructure, although a few larger features appear near the ion-stopping peak where the conditions for self-assembly due to stochastic Co–Co interactions are the most favorable. In this case, any nanoclusters formed during the implantation have sizes that are moderated by the competition between short-range chemical diffusion of energetic species and ion-beam damage which fragments growing particle diameters, limiting overall sizes.¹⁹ The latter leads to so-called “inverse Ostwald ripening” process theorized to produce very small nanoclusters.^{19,41} In our sample, the largest observable features are seen at the peak ion-beam stopping profile, and there appear to a great deal of cobalt that is present in unresolved features smaller than (1 nm). This is particularly true in regions at ± 15 nm from the fluence peak where there is no visual evidence in the TEM for cluster formation although the EDX, XPS, and SIMS mapping does show a substantial cobalt concentration with unresolved feature sizes. Furthermore, the neutron data establishes that there are clearly some magnetic Co^0 and Co^{2+} in these “wing” regions, supporting the theoretical ion-stopping profile. It is also noteworthy that the polarized neutrons show that such dilute regions are responsible for the highest magnetic moments $> 2 \mu_B$, whereas the Co-rich layers generate moments close to that of standard Co metal ($1.7 \mu_B$). Clearly the novel magnetic environment is mostly localized to the dilute regions, indicating the role of ultrasmall defect structures. While matrix-isolated cobalt are produced at low ion fluences,¹⁷ the growth of larger defect clusters is presumably favored above a threshold Co ion concentration. Thus, we studied the effect of ion beam doses on the magnetic properties more closely.

Several samples were prepared with different cobalt ion doses. Figure 6 illustrates that a threshold fluence is required to generate the observable magnetization, which only appears for samples containing 6% or more average Co in the implanted region. Complementary X-ray reflectometry using Cu $K\alpha$ radiation is overlaid with the neutron patterns in Figure 6. The systematic increase in the critical edge of the X-ray reflection confirms that higher Co concentrations are incorporated in proportion to the increased ion dose, which are detectable because the Co species makes a large contribution to the overall electron density. Samples with lower percentages of Co (Figure 6a,b) did not yield an observable neutron spin asymmetry. The lack of a SA signal in the lightly doped samples favors the interpretation that small self-assembled clusters, rather than matrix-isolated Co species, are the dominant source of the room temperature magnetic moments because the assembly mechanism for nanoclusters is favored at higher doses. If any magnetic signal exists for the low-dose scenario, corresponding to random distribution of matrix-isolated cobalt,¹⁷ it is hidden in our samples beneath the statistical error of PNR patterns Figure 6a,b, whereas the higher doses result in a clear magnetic signal (Figure 6c,d). This agrees closely with recent work showing that the magnetic signal of lightly doped amorphous TiO_2 is intrinsically weak.¹⁷ On the basis of the statistical uncertainty in the neutron patterns, we can place an upper limit

on the dilute magnetic Co in either the Co^0 or Co^{2+} state (i.e., via the so-called the intrinsic mechanism) at $0.2 \mu_B$ per cobalt at 300 K. Collectively, this analysis implies that it is desirable to control the formation of small defect clusters embedded during the ion beam synthesis, as this potentially allows a multifunctional range of magnetizations from areas with small intrinsic effects interposed between highly magnetic nanocomposite regions. On the other hand, it is unclear what fundamental mechanism allows ultrasmall defect clusters to produce such large magnetizations in the 3D host. On general theoretical grounds, magnetic moments of $> 2 \mu_B$ per Co are only expected in low symmetry environments for free-standing clusters or at a surface region where orbital momentum is conserved and the bulk electronic band structure is modified. Thus, a subtle mechanism must be at work in the Co: TiO_2 nanocomposites, leading to conditions that favor large effective magnetic moments. This may, for instance, involve the cooperation between cobalt acting to polarize spin-bearing defects in the surrounding titania. It is thus interesting that the strongest magnetization in our case correlates with the volume segments in the films which are quite structurally defective and far from the pure stoichiometry of the TiO_2 . The interplay between the magnetism and structural defects in DMOS materials has been proposed several times.^{3,9,22,34} For instance, it has been noted that the occurrence of ferromagnetism correlates strongly with the presence of grain boundary regions in the case of polycrystalline ZnO ⁴² and TiO_2 ,⁶ along with oxygen vacancies and structural disorder.³ Such observations have led to the rebirth of the field of defect ferromagnetism.¹¹ On the other hand, direct experimental evidence regarding the nature of the specific defects has been lacking. To this end, it is useful to consider the variation in stoichiometry and mass densities extracted from the reflectometry of the Co: $\text{TiO}_{2-\delta}$ so as to assess how this is correlated with the local defect structure detected with positron annihilation lifetime spectroscopy.

The neutron and X-ray reflectometry show that the oxygen concentration and mass density are variable across the implanted region of the Co: $\text{TiO}_{2-\delta}$ films, indicating that metallic clustering drives additional chemical defects and distortion in the surrounding $\text{TiO}_{2-\delta}$ host. To understand the effect of the Co metal incorporation, it is vital to analyze the X-ray reflectometry because it provides information that is complementary to the neutron data set. The off-resonant X-ray SLD (ρ_x) which determines the XR reflection pattern has the same general form as the neutron ρ_n :

$$\rho_x = r_e \sum_{i=0}^{i=J} N f_i \quad (6)$$

where f_i is the X-ray form factor and $r_e = 2.81 \times 10^{-5} \text{ \AA}$ is the classical electron radius. While identical mathematic techniques are thus used to refine the X-ray data, the physical information that is encoded is quite different. The X-ray form factors (f_i) are closely related to the atomic electron density, whereas the neutron's b_i are uncorrelated with the electron density and show disproportionately high sensitivity to certain low Z elements such as oxygen. For this reason, a comparison of the values of ρ_x and ρ_n reveals useful information about the metallic and oxygen concentration in the samples, respectively. Prior to the implantation step, the reflectometry of the Co-free $\text{TiO}_{2-\delta}$ films is connected with a homogeneous $\text{TiO}_{2-\delta}$ layer, giving a SLD equal to $\rho_x = (30.8 \pm 1) \times 10^{-6} \text{ \AA}^{-2}$ for the X-rays and $\rho_n = (2.2 \pm 0.1) \times 10^{-6} \text{ \AA}^{-2}$ for the neutrons. These values are

Figure 7. (a) Positron annihilation lifetime spectroscopy for a pure TiO₂ film, and a TiO₂ film implanted with 10% Co. (b) Fitted positron lifetime and peak X-ray scattering length density for various samples showing densification of the transition-metal lattice. (c) Schematic of the proposed defect scheme and its dependence on the ion-implantation process.

reasonably close to those expected for crystalline TiO₂ rutile where ρ_x/ρ_m is 32.5/2.5 (both in units of $10^{-6} \text{ \AA}^{-2}$). The lower absolute values of ρ_x and ρ_n for the amorphous starting films indicates a mass density that is reduced between 5–10% compared to rutile (i.e., giving lower N_{Ti} and N_{O}), which is typical for the amorphous phase. On the other hand, the exact ratio of the ρ_x/ρ_n can be analyzed closely by simultaneously solving for common variables N_{Ti} and N_{O} in ρ_n in eq 4 with ρ_x in eq 6, using the two experimentally known variables (ρ_x, ρ_n) to give a unique solution. This indicates that the oxygen content is reduced to TiO_(1.9 ± 0.05) in the starting amorphous film, as a result of the low deposition temperature, and this also explains the observed ρ_n because oxygen makes the dominant contribution to the neutron scattering length density ($b_{\text{O}} = 5.803 \text{ fm}$, $b_{\text{Ti}} = -3.483 \text{ fm}$, $b_{\text{Co}} = 2.49 \text{ fm}$). Following a similar analysis through the series of implanted samples, it is clear that the ion beam synthesis has an interesting effect: the values of ρ_x are moderately increased to a maximum of $36 \times 10^{-6} \text{ \AA}^{-2}$ in the heaviest implanted regions, where the neutron ρ_n is reduced in the same regions. Qualitatively, this implies that ion implantation of Co produces a local increase in the metal content accompanied by a simultaneous loss in the oxygen content. If the fitted ρ_x/ρ_m ratios are quantitatively analyzed for the implanted regions in 10% Co:TiO_{2-δ} (using the $N_{\text{Ti}}:N_{\text{Co}}$ information from XPS or SRIM calculations), this implies that the oxygen content has a minima giving a composite described as Co:TiO_(1.75 ± 0.10). The noncontact reflectometry measurements thus confirm the general features directly noted in the XPS (Figure 5b). The loss of oxygen is not unexpected and occurs for several reasons in the implanted region. Under chemical and thermal equilibrium, the substitution of a Ti⁴⁺ with Co²⁺ within TiO₂ requires the formation of the charge-compensating oxygen vacancy in order to be energetically viable.³ Furthermore, under nonequilibrium ion implantation, beam damage can also introduce metastable defect structures.

The latter mechanism is favored by the Monte Carlo SRIM calculations (Figure 4c), which imply that the lowest neutron SLD values, i.e., the strongest degree of oxygen modification, and peak magnetic moment, both coincide with the highest degree of ion-induced oxygen displacements. In addition to the modulation of the oxygen content, the SLDs in the implanted layer are influenced by a reduction in the net atomic density ($N = N_{\text{Ti}} + N_{\text{Co}} + N_{\text{O}}$), which is lowered by 5–15% compared to the nonimplanted regions, as shown by application of eqs 6 and 4 to the observed profiles. The reduction is partly explained by the presence of a metallic Co fraction because the atomic density of the metal is $\sim 10\%$ lower ($N = 9.0 \times 10^{28} \text{ atoms per m}^3$) compared to the oxides which have shorter metal-anion ionic bonds such as CoO ($10.3 \times 10^{28} \text{ atoms per m}^3$) or TiO₂ ($9.6 \times 10^{28} \text{ atoms per m}^3$). On the other hand, even assuming the upper limit where the entire 10–16% of Co population forms embedded metallic nanoclusters, this would only account for a $\sim 2\%$ density reduction. The extra loss of density we observe is thus significant because it implies that additional defects are created in the host material between Co-containing regions (i.e., there is an extended defect structure around the nanoclusters). This scenario is a natural consequence of displacements caused by the incoming ions. It is also supported by the structural and bond distortions that are required to accommodate the embedded nanoclusters in their locality.⁴³ On the basis of these results, there is evidence of an oxygen-deficient, low-density environment surrounding the embedded Co, which is correlated with the anomalous magnetic properties, warranting further investigation using a local probe technique.

To directly detect the volumetric size of the specific defect structures surrounding the implanted Co, we employed low-energy positron annihilation spectroscopy (PALS) on the series of Co:TiO_{2-δ} films. PALS is a technique that is particularly sensitive to open volume defects such as vacancy clusters and

microvoids.⁴⁴ Low-energy beamline experiments were performed at the Australian National University using a Surko buffer gas trap beamline, which implants a subnanosecond pulse of positrons.⁴⁵ The resultant annihilation radiation is detected as a function of time from injection. The lifetime components within each sample were determined by fitting the experimentally measured spectra $A(t)$ to

$$A(t) = R(t) \times \left[I_0 + \sum_{i=1}^n I_i \exp\left(-\frac{t}{\tau_i}\right) \right] + B \quad (7)$$

where t is time, $R(t)$ is the instrument resolution function, τ_i is the mean lifetime of the i th component, I_i is the relative intensity of the i th component, and B is the background. The decay spectra for the unimplanted sample and 10% implanted sample are notably different (Figure 7a), indicating that the lifetimes are affected by a modified defect structure caused by the Co implantation. The positrons were implanted at 2 keV, where simulations showed that the positron population is initially located within the $\text{TiO}_{2-\delta}$ thin film layer rather than film/substrate interface. The resulting positron spectra are thus representative of the $\text{TiO}_{2-\delta}$ and $\text{Co:TiO}_{2-\delta}$ layers and can be well-described using a single lifetime component (τ) in the range 200–400 ps (ps). The range of values is in general agreement with past work on nanoscale defective $\text{TiO}_{2-\delta}$.⁴⁶ The quantified lifetimes are all much lower than found in highly porous magnetic TiO_2 nanoclusters (3000 ps), which contain large voids.⁴⁶ Nevertheless, the τ s observed in all samples are slightly longer compared to the free positron τ in crystalline TiO_2 (170 ps),^{46,47} indicating relatively small micropores and open volumes in the dense structure. Systematic trends are evident in Figure 7b) across the series at different levels of Co implantation, showing that the positron lifetime is decreased as additional Co is added. As longer lifetimes are correlated with larger void sizes, this result indicates that ion-beam implantation of Co causes a reduction in size of the detectable defect pore. An increase in the relative intensity of the lifetime component is also noted for the implanted samples, suggesting that numerous smaller defects are created during implantation. The largest τ s are in the range of 250–500 ps and occur in the unimplanted amorphous samples, matching previously observed lifetimes in defective TiO_2 containing microvoids of approximately dimer and trimer size.⁴⁸ For example, inspection of crystal structure data using molecular dynamics by Kaur and Singh⁴⁹ shows that microvoids of $0.5\text{--}1\text{ nm}^3$ are present in some regions of the amorphous titania phases as a consequence of the reduced mass density (Figure 7c), and these feature sizes correspond to the longer positron lifetimes. In contrast, the positron lifetimes are lower in the Co-implanted samples, indicating that the open-volume defect clusters are significantly smaller (i.e., much less than 1.0 nm^3). Indeed, the lifetimes for the highest dose samples approach the equivalent values known for A-site Ti monovacancies in crystalline $\text{TiO}_{2-\delta}$ (190–220 ps). Overall, this shows that implantation leads to filling in of dimer and trimer sized voids in the $\text{TiO}_{2-\delta}$ host via occupation with Co and other displaced ions. The resulting densification correlates well with the increase in electron density detected from the X-ray reflectometry fits (Figure 7b), leading us to propose the evolution of the defect structure shown schematically in Figure 7c. In this sequence, the filling in of negatively charged microvoids with positive ions results in Co-decorated defect complexes, which are surrounded by an increased fraction of oxygen vacancies. The starting microvoids are so

small that they can only accommodate 1–10 Co atoms. If further Co self-assembles around the “seed” cluster, it must displace or substitute surrounding oxygen and titanium. Clearly the local chemical environment around such a void-initiated cluster will be highly nonsymmetric and will contain local chemistry analogous to titanium and oxygen vacancies familiar from crystalline forms of TiO_2 . It appears that this local structure, which has many features in common with disordered grain boundary regions, is a strong candidate to explain the large magnetization of the Co. It is interesting to speculate whether the crystal fields in such a disordered environment can fully quench the angular and spin magnetic moment. First principle calculations and X-ray circular dichroism measurements could assess this in the future.

■ CONCLUSION

High magnetizations are achievable in $\text{Co:TiO}_{2-\delta}$ nanocomposites using ion beam synthesis, and the functional properties can be optimized by controlling the formation of small embedded nanoclusters in the semiconducting host. The macroscopic magnetic properties of such oxides exhibit key signatures of “ferromagnetism”, including nonlinear field response and hysteresis. The rich nanoscale complexity in such systems necessitates the usage of magnetic characterization techniques that have depth resolution or sensitivity to local magnetic fields. Our result is a first effort to use polarized neutron reflectometry to quantitatively understand the magnetization in dilute magnetic oxide $\text{Co:TiO}_{2-\delta}$ nanocomposites. On the basis of this, we find no evidence of d^0 magnetism, indicating that interfaces and lattice defects produce negligible magnetic properties by themselves. Instead, the large spin-dependent neutron scattering in the Co-rich samples provides indisputable experimental evidence of strong magnetism that is tied to the local structure surrounding the Co atoms. Intriguingly, although we observe features usually tied to metallic clustering, the magnetic moments cannot be explained by the standard argument of the precipitation of conventional metallic nanoclusters. Instead, the results imply a novel form of ultrasmall defect cluster embedded within the disordered oxide host surrounded by a complex defect structure. It appears that the nanocluster–matrix interfaces and the disorder within the host titania have a strong effect on the magnetic spin polarization. It is noteworthy that the Anomalous Hall Effect does sometimes appear in magnetically inhomogeneous samples containing clusters,^{4,11} indicating that such materials may be potentially suitable for a narrow range of applications, particularly where high mobility transport is not a constraint. However, it remains desirable to produce a more homogeneous magnetic state. To this end, one promising method with ion beam synthesis is to use multiple implant steps with different beam energies to generate more homogeneous cobalt distributions as previously demonstrated,¹⁷ followed by subsequent bombardment in order to control the ion beam damage profile (i.e., vacancies).⁵⁰ Before such work can be undertaken, the precise details of the electronic state responsible for the large magnetization warrant further investigation. Taken collectively, these results are an important step toward understanding the magnetic variability of the dilute magnetic oxide materials, indicating both the challenges and opportunities presented by the deliberate or accidental formation of ultrasmall nanocrystals. Defect engineering of embedded cobalt clusters via ion beam implantation offers a

promising method to generate the high local magnetizations necessary for multifunctional components in spintronics.

METHODS

Film preparation: $\text{TiO}_{2-\delta}$ films (68 nm) were deposited on 100 Si wafers using a viscous flow atomic layer deposition (ALD) reactor (ASM Microchemistry F-120) at 393 K to provide amorphous thin films as the starting template to provide the maximum degree of local structural disorder without grain boundaries. The films were deposited by exposing the Si substrates to sequential pulses of TiCl_4 (0.4 s) and H_2O (1.0 s) in N_2 carrier gas, which was also used to purge the deposition chamber between each precursor pulse. Selected films were subsequently implanted with Co ions using an ion implanter equipped with a metal vapor vacuum arc (MEVVA) ion source.⁵¹ The extraction voltage in all cases was 20 kV and the applied implant doses were in the range of $0.3\text{--}2.0 \times 10^{16}$ ions cm^{-2} . MEVVA sources generate Co^+ (34%), Co^{2+} (59%), and Co^{3+} (7%) ion charge states, thus the implanted energy was selected to localize the Co in the $\text{TiO}_{2-\delta}$ with negligible overlap with the underlying substrate. No annealing step was performed to minimize thermally induced crystallization, segregation, and diffusion and the data presented is for the films in their as-prepared state.

X-ray diffraction and X-ray reflectometry (XRR) were performed on a Panalytical X'Pert Pro using $\text{Cu K}\alpha$ radiation. Magnetic properties were performed on a Quantum Design PPMS. Transmission electron microscopy was performed on a JEOL 2200FS (operated at 200 keV) fitted with a Gatan image filter (GIF) and energy dispersive X-ray spectrometer (EDX).

Polarized neutron reflectometry used the time-of-flight PLATYPUS reflectometer at ANSTO (Sydney, Australia)²⁵ and the monochromatic NREX reflectometer at FRMII (Munich, Germany), where the spin up and down reflectivity channels were each collected for 6–12 h across a variety of scattering angles.

XPS was conducted on the same sample, implanted with an average of 10% Co, using a Thermo Scientific ESCALAB250Xi instrument with $\text{Al K}\alpha$ radiation and variable-time etching by exposure to 3 keV argon.

Beamline PALS experiments were performed at The Australian National University using a Surko buffer gas trap beamline, which implants a sub-nanosecond pulse of positrons into the desired target at energies up to 20 keV. The resultant annihilation radiation was detected with a BaF_2 detector as a function of time from injection, and the lifetime spectrum was analyzed to get information about the open volumes contained within the sample. Details of the experimental apparatus are described in ref 45. The 10 mm $\times$ 10 mm samples were mounted on a stainless steel stub and measured with beam energies of 2 and 3 keV.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsami.6b15071.

Details of the fitting procedure used for the neutron reflectometry refinement; method used to determine the uncertainty limits on the magnetic moments; examples of alternate magnetic scattering models which can be ruled out; Rutherford-backscattering experimental data and contrast-adjusted TEM images (PDF)

AUTHOR INFORMATION

Corresponding Author

*E-mail: dcortie@uow.edu.au.

ORCID

David L. Cortie: 0000-0003-2383-1619

James P. Sullivan: 0000-0003-4489-4926

Author Contributions

D.L.C., F.K., G.T., and P.E. designed the experiment. G.T. and P.E. synthesized the thin films. X.W. and D.L.C. performed initial characterization of the samples. Y.K. and T.K. conducted the polarized neutron experiment at FRMII. D.L.C., M.J., A.P.L.B., S.C., and J.L.B. performed the polarized neutron and X-ray reflectometry experiments at ANSTO. D.L.C. analyzed the PNR data. R.A. conducted the TEM study. J.P.S., D.S., and J.P.H. conducted the low-energy positron experiment. D.S. analyzed the PALS data. D.L.C. and F.K. cowrote the manuscript. All authors helped edit the manuscript.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

D.L.C. and J.L.B. acknowledge the support of the Australian Institute Nuclear Science and Engineering. We also acknowledge the support of the ARC Centres of Excellence program.

REFERENCES

- (1) Waldrop, M. M. The Chips are Down for Moore's Law. *Nature* **2016**, *530*, 144–147.
- (2) Matsumoto, Y.; Murakami, M.; Shono, T.; Hasegawa, T.; Fukumura, T.; Kawasaki, M.; Ahmet, P.; Chikyow, T.; Koshihara, S.-y.; Koinuma, H. Room-Temperature Ferromagnetism in Transparent Transition Metal-Doped Titanium Dioxide. *Science* **2001**, *291* (5505), 854–856.
- (3) Griffin Roberts, K.; Varela, M.; Rashkeev, S.; Pantelides, S. T.; Pennycook, S. J.; Krishnan, K. M. Defect-Mediated Ferromagnetism in Insulating Co-doped Anatase TiO_2 Thin Films. *Phys. Rev. B: Condens. Matter Mater. Phys.* **2008**, *78* (1), 014409.
- (4) Shinde, S. R.; Ogale, S. B.; Higgins, J. S.; Zheng, H.; Millis, A. J.; Kulkarni, V. N.; Ramesh, R.; Greene, R. L.; Venkatesan, T. Co-occurrence of Superparamagnetism and Anomalous Hall Effect in Highly Reduced Cobalt-Doped Rutile $\text{TiO}_{2-\delta}$ Films. *Phys. Rev. Lett.* **2004**, *92* (16), 166601.
- (5) Santara, B.; Pal, B.; Giri, P. K. Signature of Strong Ferromagnetism and Optical Properties of Co doped TiO_2 nanoparticles. *J. Appl. Phys.* **2011**, *110* (11), 114322.
- (6) Bryan, J. D.; Santangelo, S. A.; Kevenen, S. C.; Gamelin, D. R. Activation of High- T_C Ferromagnetism in $\text{Co}^{2+}:\text{TiO}_2$ and $\text{Cr}^{3+}:\text{TiO}_2$ Nanorods and Nanocrystals by Grain Boundary Defects. *J. Am. Chem. Soc.* **2005**, *127* (44), 15568–15574.
- (7) Zhao, T.; Shinde, S. R.; Ogale, S. B.; Zheng, H.; Venkatesan, T.; Ramesh, R.; Das Sarma, S. Electric Field Effect in Diluted Magnetic Insulator Anatase Co: TiO_2 . *Phys. Rev. Lett.* **2005**, *94* (12), 126601.
- (8) Toyosaki, H.; Fukumura, T.; Yamada, Y.; Nakajima, K.; Chikyow, T.; Hasegawa, T.; Koinuma, H.; Kawasaki, M. Anomalous Hall effect governed by electron doping in a room-temperature transparent ferromagnetic semiconductor. *Nat. Mater.* **2004**, *3* (4), 221–224.
- (9) Ogale, S. B. Dilute Doping, Defects, and Ferromagnetism in Metal Oxide Systems. *Adv. Mater.* **2010**, *22* (29), 3125–3155.
- (10) Chambers, S. A.; Droubay, T.; Wang, C. M.; Lea, A. S.; Farrow, R. F. C.; Folks, L.; Deline, V.; Anders, S. Clusters and Magnetism in Epitaxial Co-doped TiO_2 Anatase. *Appl. Phys. Lett.* **2003**, *82* (8), 1257–1259.
- (11) Akdogan, N.; Nefedov, A.; Zabel, H.; Westerholt, K.; Becker, H.-W.; Somsen, C.; Gök, Ş.; Bashir, A.; Khaibullin, R.; Tagirov, L. High-temperature Ferromagnetism in Co-implanted TiO_2 rutile. *J. Phys. D: Appl. Phys.* **2009**, *42* (11), 115005.
- (12) Yamada, Y.; Ueno, K.; Fukumura, T.; Yuan, H. T.; Shimotani, H.; Iwasa, Y.; Gu, L.; Tsukimoto, S.; Ikuhara, Y.; Kawasaki, M. Electrically Induced Ferromagnetism at Room Temperature in Cobalt-Doped Titanium Dioxide. *Science* **2011**, *332* (6033), 1065–1067.
- (13) Toyosaki, H.; Fukumura, T.; Ueno, K.; Nakano, M.; Kawasaki, M. A Ferromagnetic Oxide Semiconductor as Spin Injection Electrode in Magnetic Tunnel Junction. *Jpn. J. Appl. Phys.* **2005**, *44* (2), 28–32.

- (14) Coey, J. M. D.; Venkatesan, M.; Fitzgerald, C. B. Donor Impurity Band Exchange in Dilute Ferromagnetic Oxides. *Nat. Mater.* **2005**, *4* (2), 173–179.
- (15) Sprouster, D. J.; Giulian, R.; Araujo, L. L.; Kluth, P.; Johannessen, B.; Cookson, D. J.; Foran, G. J.; Ridgway, M. C. Structural and Vibrational Properties of Co Nanoparticles Formed by Ion Implantation. *J. Appl. Phys.* **2010**, *107* (1), 014313.
- (16) Jacobsohn, L. G.; Hawley, M. E.; Cooke, D. W.; Hundley, M. F.; Thompson, J. D.; Schulze, R. K.; Nastasi, M. Synthesis of Cobalt Nanoparticles by Ion Implantation and Effects of Postimplantation Annealing. *J. Appl. Phys.* **2004**, *96* (8), 4444–4450.
- (17) Yildirim, O.; Cornelius, S.; Smekhova, A.; Zykov, G.; Gan'shina, E. A.; Granovsky, A. B.; Hübner, R.; Bähz, C.; Potzger, K. The Local Environment of Cobalt in Amorphous, Polycrystalline and Epitaxial Anatase TiO₂:Co Films Produced by Cobalt Ion Implantation. *J. Appl. Phys.* **2015**, *117* (18), 183901.
- (18) Leedahl, B.; Zatspein, D. A.; Boukhvalov, D. W.; Kurmaev, E. Z.; Green, R. J.; Zhidkov, I. S.; Kim, S. S.; Cui, L.; Gavrilov, N. V.; Cholak, S. O.; Moewes, A. Study of the Structural Characteristics of 3d Metals Cr, Mn, Fe, Co, Ni, and Cu Implanted in ZnO and TiO₂—Experiment and Theory. *J. Phys. Chem. C* **2014**, *118* (48), 28143–28151.
- (19) Yuan, C. W.; Yi, D. O.; Sharp, I. D.; Shin, S. J.; Liao, C. Y.; Guzman, J.; Ager, J. W.; Haller, E. E.; Chrzan, D. C. Theory of Nanocluster Size Distributions from Ion Beam Synthesis. *Phys. Rev. Lett.* **2009**, *102* (14), 146101.
- (20) Griffin, K. A.; Pakhomov, A. B.; Wang, C. M.; Heald, S. M.; Krishnan, K. M. Intrinsic Ferromagnetism in Insulating Cobalt Doped Anatase TiO₂. *Phys. Rev. Lett.* **2005**, *94* (15), 157204.
- (21) Ohtsuki, T.; Chainani, A.; Eguchi, R.; Matsunami, M.; Takata, Y.; Taguchi, M.; Nishino, Y.; Tamasaku, K.; Yabashi, M.; Ishikawa, T.; Oura, M.; Senba, Y.; Ohashi, H.; Shin, S. Role of Ti 3d Carriers in Mediating the Ferromagnetism of Co:TiO₂ Anatase Thin Films. *Phys. Rev. Lett.* **2011**, *106* (4), 047602.
- (22) Coey, J. M. D.; Stamenov, P.; Gunning, R. D.; Venkatesan, M.; Paul, K. Ferromagnetism in Defect-Ridden Oxides and Related Materials. *New J. Phys.* **2010**, *12* (5), 053025.
- (23) Fitzsimmons, M. R., Application of Polarized Neutron Reflectometry to Studies of Artificially Structured Magnetic Materials. In *Modern Techniques for Characterizing Magnetic Materials*; Zhu, Y., Ed.; Springer: Boston, MA, 2005; pp 107–155.
- (24) Maruyama, T.; Ohtsuki, T.; Sakai, E.; Abe, H.; Shimada, T.; Hasegawa, T.; Nagamatsu, S.-i.; Fujikawa, T. Multiple-scattering Approach to Ti L_{2,3}-edge XMCD analyses for Co doped TiO₂. *J. Phys.: Conf. Ser.* **2009**, *190* (1), 012018.
- (25) Saerbeck, T.; Klose, F.; Le Brun, A. P.; Füzi, J.; Brule, A.; Nelson, A.; Holt, S. A.; James, M. Polarization “Down Under”: The Polarized Time-of-Flight Neutron Reflectometer PLATYPUS. *Rev. Sci. Instrum.* **2012**, *83* (8), 081301.
- (26) Saoudi, M.; Fritzsche, H.; Nieuwenhuys, G. J.; Hesselberth, M. B. S. Size Effect in the Spin Glass Magnetization of Thin AuFe Films as Studied by Polarized Neutron Reflectometry. *Phys. Rev. Lett.* **2008**, *100* (5), 057204.
- (27) Cortie, D. L.; Lin, K. W.; Shueh, C.; Hsu, H. F.; Wang, X. L.; James, M.; Fritzsche, H.; Brück, S.; Klose, F. Exchange bias in a nanocrystalline hematite/permalloy thin film investigated with polarized neutron reflectometry. *Phys. Rev. B: Condens. Matter Mater. Phys.* **2012**, *86* (5), 054408.
- (28) Bertinshaw, J.; Brück, S.; Lott, D.; Fritzsche, H.; Khaydukov, Y.; Soltwedel, O.; Keller, T.; Goering, E.; Audehm, P.; Cortie, D. L.; Hutchison, W. D.; Ramasse, Q. M.; Arredondo, M.; Maran, R.; Nagarajan, V.; Klose, F.; Ulrich, C. Element-specific Depth Profile of Magnetism and Stoichiometry at the La_{0.67} Sr_{0.33} MnO₃/BiFeO₃ interface. *Phys. Rev. B: Condens. Matter Mater. Phys.* **2014**, *90* (4), 041113.
- (29) Gambardella, P.; Rusponi, S.; Veronese, M.; Dhesi, S. S.; Grazioli, C.; Dallmeyer, A.; Cabria, I.; Zeller, R.; Dederichs, P. H.; Kern, K.; Carbone, C.; Brune, H. Giant Magnetic Anisotropy of Single Cobalt Atoms and Nanoparticles. *Science* **2003**, *300* (5622), 1130–1133.
- (30) Biersack, J. P.; Haggmark, L. G. A Monte Carlo Computer Program for the Transport of Energetic Ions in Amorphous Targets. *Nucl. Instrum. Methods* **1980**, *174* (1-2), 257–269.
- (31) Nelson, A. Co-refinement of Multiple-contrast Neutron/X-ray Reflectivity Data using MOTOFIT. *J. Appl. Crystallogr.* **2006**, *39* (2), 273–276.
- (32) Doan, T.-D.; Fermon, C.; Humbert, P.; Leymarie, E. *SimulReflec: Reflectivity Curve Simulations and Fitting*; CEA Saclay: Gif sur Yvette, France, 2011; <http://www-llb.cea.fr/prism/programs/simulreflec/simulreflec.html>.
- (33) Parras, M.; Varela, Á.; Cortés-Gil, R.; Boulahya, K.; Hernando, A.; González-Calbet, J. M. Room-Temperature Ferromagnetism in Reduced Rutile TiO_{2-δ} Nanoparticles. *J. Phys. Chem. Lett.* **2013**, *4* (13), 2171–2176.
- (34) Zhou, S.; Čížmár, E.; Potzger, K.; Krause, M.; Talut, G.; Helm, M.; Fassbender, J.; Zvyagin, S. A.; Wosnitza, J.; Schmidt, H. Origin of Magnetic Moments in Defective TiO₂ Single Crystals. *Phys. Rev. B: Condens. Matter Mater. Phys.* **2009**, *79* (11), 113201.
- (35) Coey, J. M. D. d₀ Ferromagnetism. *Solid State Sci.* **2005**, *7* (6), 660–667.
- (36) Cortie, D. L.; Brown, J. D.; Brück, S.; Saerbeck, T.; Evans, J. P.; Fritzsche, H.; Wang, X. L.; Downes, J. E.; Klose, F. Intrinsic Reduction of the Ordered 4f Magnetic Moments in Semiconducting Rare-earth Nitride Thin Films: DyN, ErN, and HoN. *Phys. Rev. B: Condens. Matter Mater. Phys.* **2014**, *89* (6), 064424.
- (37) Dinega, D. P.; Bawendi, M. G. A Solution-Phase Chemical Approach to a New Crystal Structure of Cobalt. *Angew. Chem., Int. Ed.* **1999**, *38* (12), 1788–1791.
- (38) Peredkov, S.; Neeb, M.; Eberhardt, W.; Meyer, J.; Tombers, M.; Kampschulte, H.; Niedner-Schatteburg, G. Spin and Orbital Magnetic Moments of Free Nanoparticles. *Phys. Rev. Lett.* **2011**, *107* (23), 233401.
- (39) Saadaoui, H.; Luo, X.; Salman, Z.; Cui, X. Y.; Bao, N. N.; Bao, P.; Zheng, R. K.; Tseng, L. T.; Du, Y. H.; Prokscha, T.; Suter, A.; Liu, T.; Wang, Y. R.; Li, S.; Ding, J.; Ringer, S. P.; Morenzoni, E.; Yi, J. B. Intrinsic Ferromagnetism in the Diluted Magnetic Semiconductor Co:TiO₂. *Phys. Rev. Lett.* **2016**, *117* (22), 227202.
- (40) Silva, N. J. O.; Puente-Orench, I.; Martins, M.; Trindade, T.; Millán, A.; Campo, J.; Palacio, F. Neutron Diffraction and Magnetism of CoO Antiferromagnetic Nanoparticles. *J. Phys.: Conf. Ser.* **2011**, *325* (1), 012020.
- (41) Heinig, K. H.; Müller, T.; Schmidt, B.; Strobel, M.; Möller, W. Interfaces under ion irradiation: growth and taming of nanostructures. *Appl. Phys. A: Mater. Sci. Process.* **2003**, *77* (1), 17–25.
- (42) Tietze, T.; Audehm, P.; Chen, Y. C.; Schütz, G.; Straumal, B. B.; Protasova, S. G.; Mazilkin, A. A.; Straumal, P. B.; Prokscha, T.; Luetkens, H.; Salman, Z.; Suter, A.; Baretzky, B.; Fink, K.; Wenzel, W.; Danilov, D.; Goering, E. Interfacial Dominated Ferromagnetism in Nanograined ZnO: a μ SR and DFT study. *Sci. Rep.* **2015**, *5*, 8871.
- (43) Sprouster, D. J.; Ridgway, M. C. Ion Beam Formation and Modification of Cobalt Nanoparticles. *Appl. Sci.* **2012**, *2* (2), 396–442.
- (44) Schultz, P. J.; Lynn, K. G. Interaction of positron beams with surfaces, thin films, and interfaces. *Rev. Mod. Phys.* **1988**, *60* (3), 701–779.
- (45) Sullivan, J. P.; Roberts, J.; Weed, R. W.; Went, M. R.; Newman, D. S.; Buckman, S. J. A Trap-Based Positron Beamline for the Study of Materials. *Meas. Sci. Technol.* **2010**, *21* (8), 085702.
- (46) Ghosh, S.; Khan, G. G.; Mandal, K.; Samanta, A.; Nambissan, P. M. G. Evolution of Vacancy-Type Defects, Phase Transition, and Intrinsic Ferromagnetism during Annealing of Nanocrystalline TiO₂ Studied by Positron Annihilation Spectroscopy. *J. Phys. Chem. C* **2013**, *117* (16), 8458–8467.
- (47) Valeeva, A. A.; Rempel, A. A.; Sprengel, W.; Schaefer, H. E. Vacancies on the Ti sublattice in Titanium Monoxide TiO_y Studied Using Positron Annihilation Techniques. *Phys. Rev. B: Condens. Matter Mater. Phys.* **2007**, *75* (9), 094107.

- (48) Zheng, F.; Liu, Y.; Liu, Z.; Dai, Y. Q.; Fang, P. F.; Wang, S. J. Study on Defect Properties of Nanocrystalline TiO_2 During Phase Transition by Positron Annihilation Lifetime. *J. Cryst. Growth* **2012**, 353 (1), 55–58.
- (49) Kaur, K.; Singh, C. V. Amorphous TiO_2 as a Photocatalyst for Hydrogen Production: A DFT Study of Structural and Electronic Properties. *Energy Procedia* **2012**, 29, 291–299.
- (50) Stiller, M.; Barzola-Quiquia, J.; Esquinazi, P.; Spemann, D.; Meijer, J.; Lorenz, M.; Grundmann, M. Strong Out-of-plane Magnetic Anisotropy in Ion Irradiated Anatase TiO_2 Thin Films. *AIP Adv.* **2016**, 6 (12), 125009.
- (51) Brown, I. G. Vacuum Arc Ion Sources. *Rev. Sci. Instrum.* **1994**, 65 (10), 3061–3081.