P H Y S I C A L   R E V I E W   L E T T E R S

Intrinsic Ferromagnetism in Insulating Cobalt Doped Anatase TiO$_2$

K. A. Griffin,[1] A. B. Pakhomov,[1] C. M. Wang,[2] S. M. Heald,[2] and Kannan M. Krishnan[1,*]

[1]*Department of Materials Science and Engineering, University of Washington, Seattle, Washington 98195, USA*
[2]*Fundamental Science Division, Pacific Northwest National Laboratory, P.O. Box 999, Richland, Washington 99352, USA*

Using complementary experiments we show that the room temperature ferromagnetism observed in anatase Co:TiO$_2$ films is not carrier mediated, but coexists with the dielectric state. TEM and x-ray absorption spectroscopy reveal a solid solution of Co in anatase, where Co is not metallic but in the $+2$ state substituting for Ti. Measurements at 300 K yield a M_S of 1.1 μ_B/Co atom, while all films are highly insulating. The evidence of intrinsic ferromagnetism in the dielectric ground state of Co:TiO$_2$ leads to new considerations for the origin of ferromagnetism in transition metal doped oxides.

PACS numbers: 75.70.-i, 85.75.-d

Since the discovery of room temperature ferromagnetism in Co doped anatase TiO$_2$ [1], there has been much focus on the Co:TiO$_2$ system [2–6] as a potential dilute magnetic semiconductor (DMS) to provide efficient injection of spin-polarized carriers for semiconductor spin-electronic devices. Some reports thus far on both anatase and rutile Co:TiO$_2$ have shown nonuniformity in films due to Co metal clustering [3–6], indicating that the film growth and post-growth processing play a crucial role in the electronic state and distribution of the Co ions in the material. Co:TiO$_2$ systems that have confirmed the absence of Co metal clusters show that anatase Co:TiO$_2$ exhibits ferromagnetic behavior above room temperature with n-type semiconducting properties [1,2,5,7]. Although a correlation of ferromagnetism with conduction is observed in these materials, the origin of ferromagnetism, its relation to the presence of free carriers, and, most importantly, whether the carriers are spin-polarized in these oxide compounds are still under much debate [8]. The most studied DMS systems are characterized by sp-d exchange between the s, p free carriers, and the d states of the transition metal dopant [9]. Because of these interactions, the carriers are spin-polarized and able to mediate ferromagnetic ordering of the magnetic moments of transition metal ions doped into the semiconductor lattice [10]. This results in correlation of ferromagnetism with carrier concentration and provides conditions for using the material as an effective spin injector [11]. Based on this criterion, only a few materials such as the p-type compounds Mn:GaAs, Mn:InAs, and Cr:ZnTe [10–12] have been reliably proven to be true DMS. The d-d double exchange due to hopping between transition metal d states (which has been well developed for mixed-valence manganites [13]) is another mechanism which can result in the DMS state, Mn:CuO being one possible example [14]. Unfortunately, all these DMS's have relatively low Curie temperatures (T_C), reducing their practical usefulness. Anatase Co:TiO$_2$ is one of the most prominent of the class of wide band gap semiconductor materials (which also includes ZnO [15], GaN [16], GaP [17], AlN [18], and SnO$_2$ [19]), that when doped with transition metal ions, remain ferromagnetic

above room temperature. It is hence of vital importance to clarify the correlation (if any) between carriers and the mechanism of ferromagnetism inherent to this structure.

In this Letter we experimentally investigate the mechanism of ferromagnetism in Co:TiO$_2$ and come to the conclusion that the presence of free carriers is not required for this material to be ferromagnetic. It can thus be referred to as a "dilute magnetic dielectric" rather than DMS, in the sense of the criteria outlined above. In previous studies, anatase Co:TiO$_2$ films grown by pulsed laser deposition [1] had moments of 0.3 μ_B/Co atom at a carrier concentration of 10^{18}/cm^3, while films grown by oxygen plasma assisted molecular beam epitaxy (OPAMBE) in an oxygen-poor atmosphere [2,20] had moments of 1.26 μ_B/Co atom at carrier concentrations of 10^{19}–10^{20}/cm^3. For insulating films grown by OPAMBE in an oxygen-rich atmosphere the spontaneous magnetization was reduced significantly [5,20]. We demonstrate that uniform films of anatase Co:TiO$_2$ can be both intrinsically ferromagnetic and highly insulating at room temperature. We suggest that previous results [1,2,5,20] correlating ferromagnetism to the carrier concentration may in fact be by-products of the creation of carriers with unbound oxygen vacancy (V_O) doping, and not directly related to the mechanism of ferromagnetism.

A series of anatase Co:TiO$_2$ films were grown by rf magnetron sputter deposition from a ceramic oxide Co$_x$Ti$_{1-x}$O$_2$ target. The base pressure of the sputter deposition chamber was 5×10^{-7} torr, and the films, ~ 85 nm thick, were grown in a pure Ar atmosphere at 4×10^{-3} torr at a deposition rate of 0.01 nm/s on matching (100) LaAlO$_3$ (LAO) substrates. The substrate temperature (T_{sub}) during deposition was 550 °C. After growth, the films were annealed for 1 h at 450 °C in ultrahigh vacuum (UHV). Structural and magnetic measurements were made on films both before and after annealing. The film structure and crystalline quality were characterized by x-ray diffraction (XRD), high resolution transmission electron microscopy (HRTEM) imaging, and selected area diffraction. Energy-dispersive x-ray spectroscopy (EDXS) data using a focused electron probe at a number of locations throughout the specimen and spectrum imaging (320 data points

over a sampling area of $\sim80 \times 100$ nm) using the Co-$L_{3,2}$ and Ti-$L_{3,2}$ edges in electron energy-loss spectroscopy, both using cross-section TEM samples, were used for detailed compositional analysis. This was complemented by Rutherford backscattering spectroscopy (RBS) for bulk analysis. Near edge x-ray absorption fine structure (NEXAFS) at the Co K edge was measured on both annealed and as-deposited Co:TiO$_2$ films to determine the oxidation state of the Co dopant in the anatase lattice. The incident x-ray beam was at an angle of $\sim1\,^\circ$ to the sample surface which provided an attenuation length of 300 nm, allowing for the entire film thickness (85 nm) to be sampled. The incident beam area on the sample surface was 5 mm by 1 mm, and the sample was rotated about the surface normal during the measurement to maximize the film volume probed. The energy calibration was monitored using a simultaneous measurement of a Co metal foil. The first peak in the derivative was taken as 7708.8 eV [21]. Magnetization (M) versus applied magnetic field (H) both at 5 and 300 K and the thermoremanent magnetization (TRM) from 5 to 365 K were measured using a Quantum Design superconducting quantum interference device (SQUID) magnetometer. Resistance of the dielectric films was measured with an electrometer and the SQUID.

The close lattice match of anatase to the LAO substrate (-0.26%) results in epitaxial growth of anatase (004), as seen by XRD measurements (Fig. 1) for as-deposited films. A comparison of the full width at half maximum (FWHM) values of XRD peak intensities of annealed and as-deposited films show an improvement in crystallinity with annealing by a $0.20\,^\circ$ decrease in the FWHM value (inset of Fig. 1). Also visible in the inset is the shift in the (004) peak to a higher angle with annealing, indicative
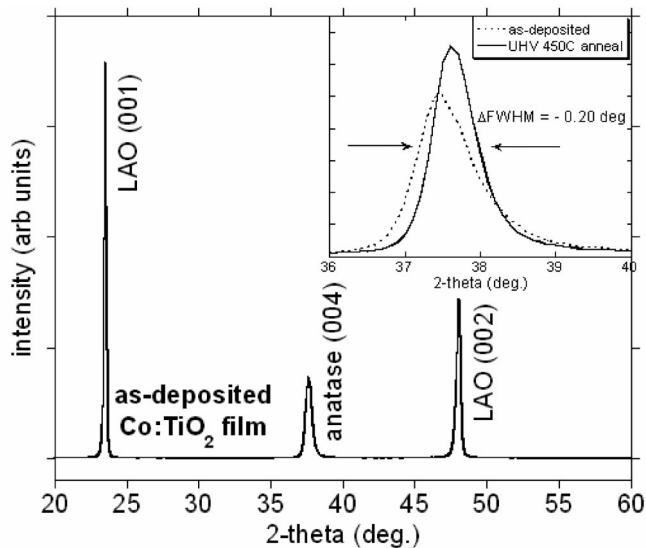
of a relaxation of the lattice along the c axis. All films were single phase with no evidence of secondary phases within the sensitivity of high-angle x-ray scattering measurements.

HRTEM imaging (Fig. 2) of cross-sectional specimens and low magnification images [inset (a) of Fig. 2] of both as-deposited and annealed films demonstrate the high quality anatase crystal structure. The inset (b) of Fig. 2 is a selected area diffraction pattern revealing single crystal (004) anatase epitaxially grown onto the LAO substrate. EDXS data taken at a number of locations throughout the specimens reveal a solid solution of Co dissolved in anatase, with Co concentrations ranging from ~2–7 at.% incorporated into the lattice. Analysis of the energy filtered images using hydrogenic cross sections also shows a uniform distribution of cobalt with an average concentration of 2.8% Co in the anatase lattice [22]. RBS measurements confirm that the bulk Co composition as a function of film depth is uniform with an average of ~2 at.% [23]. Moreover, there was no evidence for the presence of Co metal or Co-rich (above 7 at.%) anatase clusters within the films in any of these detailed TEM measurements.

NEXAFS at the Co K edge were measured on annealed and as-deposited Co:TiO$_2$ films to determine the oxidation state and local geometry of the Co dopant in the lattice. As-deposited and annealed films exhibited nearly identical NEXAFS spectra; for clarity, Fig. 3 shows only the annealed sample spectrum compared to the following reference samples: CoTiO$_3$, CoO, and Co metal. The onset of

FIG. 1. XRD of as-deposited Co:TiO$_2$ film on LAO substrate; inset: anatase (004) peak of as-deposited (dashed line) and annealed (solid line) films.
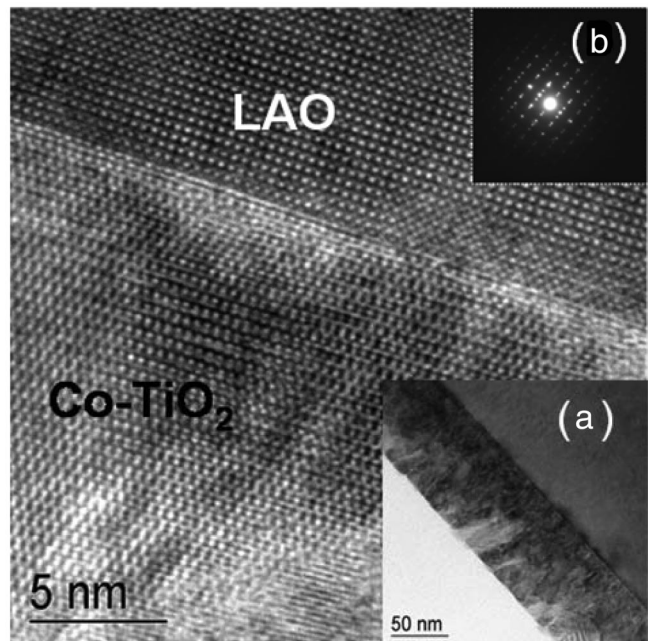

FIG. 2. High resolution TEM image from cross-sectional specimen of annealed Co:TiO$_2$ film on LAO. Inset (a) low magnification image of film (dark gray) on LAO (gray) (white area is epoxy); inset (b) selected area diffraction pattern.
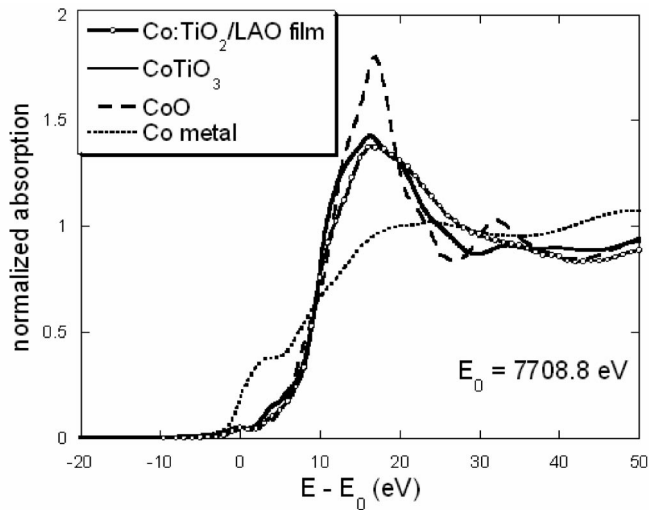
FIG. 3. Co K edge NEXAFS spectra for UHV annealed Co:TiO$_2$ film with reference samples: Co:TiO$_2$ film (open circles), CoTiO$_3$ (solid line), CoO (long dash), and Co metal (short dash) spectra.

FIG. 4. M-H loops at 300 K of as-deposited (dashed line) and UHV annealed (solid line) of Co:TiO$_2$ films. (The diamagnetic contribution from the LAO substrate has been subtracted from the experimental data.) Inset: M_R vs T of as-deposited (dashed line) and UHV annealed (solid line) films.

absorption in the NEXAFS spectra of the Co:TiO$_2$ films are a close match to CoTiO$_3$ and CoO, where Co has been interpreted to be in the $+2$ oxidation state. On the other hand, the absorption edge of Co metal is a poor match to the Co:TiO$_2$ films due to the much lower threshold energy corresponding to the Co(0) state. The closer match of NEXAFS spectrum of the sputtered Co:TiO$_2$ film to CoTiO$_3$ than to CoO is indicative of the distorted octahedral coordination of the Co atom in the lattice (i.e., Ti site in anatase), whereas in CoO the Co site has an undistorted octahedral configuration. From this comparison of Co K edge spectra it can be concluded that there is no evidence of Co metal throughout the film and Co^{2+} substitutes for Ti^{4+} in the lattice. As demonstrated in Fig. 3, the Co K edge spectra are very sensitive to the local Co environment, and Co, if present in metallic form in amounts as low as $\sim$10% of the total Co, would be detectable [24]. If ferromagnetic Co metal clusters (> 10 nm) were present, a comparison of the measured moments of 1.1 μ_B/Co atom with that of Co metal (1.7 μ_B/atom) indicates that 65% of the total Co atoms in the film would need to be Co metal to obtain the measured magnetic moments, and such a high percent of Co metal would be detectable by NEXAFS.

Magnetic hysteresis loops (M versus H) at 300 K of as-deposited and annealed Co:TiO$_2$ films in Fig. 4 show the increase in spontaneous magnetization, M_S, from 0.24 to 1.17 μ_B/Co atom with annealing. The TRM measurements (inset of Fig. 4) were measured in zero applied field after the sample was saturated, and the remanent magnetization, M_R, as a function of increasing temperature is measured [25]. The TRM results from 5 to 365 K demonstrate the enhancement of M_R from 0.07 to 0.34 μ_B/Co atom with annealing. Coercivity, H_C, also increases with
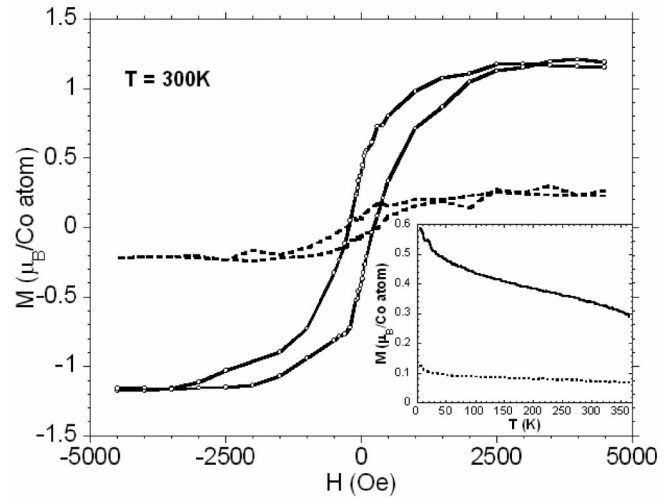
annealing, from $\sim$100 to $\sim$300 Oe. If all $\sim$2 at.% of the Co ions contribute to the measured moment, the M_S values of 1.17 μ_B/Co atom for the annealed films suggest that upon incorporation into the anatase lattice, Co^{2+} is in the low spin configuration.

The XRD experimental results suggest that the improved crystallinity of the films after UHV annealing would be the primary factor for the enhanced ferromagnetism. However, the 450 °C annealing process in UHV also provides thermal energy for the creation and diffusion of V_O's through the lattice. Despite the additional V_O formation during the UHV 450 °C anneal, all samples are highly insulating and have sheet resistances $\geq 10^{11}$ Ω/square (where this number is limited by conductance of the substrate). Thus resistivity is at least greater than 10^6 Ω cm for all samples. We therefore attribute the enhanced ferromagnetism to both the increase in crystallinity and the creation/diffusion of defects through the lattice with the annealing process. Positively charged V_O's are necessary to maintain charge neutrality as Co^{2+} substitutes for Ti^{4+}, and Coulombic attraction makes it energetically favorable for a V_O to be located in close proximity to a Co$_{Ti}^{2+}$ site. The highly nonequilibrium process of sputter deposition makes it probable that the V_O's in the as-deposited films are positioned throughout the lattice at arbitrary distances with respect to Co sites, and their number is dependent on the deposition conditions. With the creation of additional V_O's and their subsequent diffusion to Co$_{Ti}$ sites by annealing in UHV at 450 °C, the number of Co$_{Ti}^{2+}$-V_O complexes increases in correlation with the enhanced ferromagnetic signal. The high resistivity values suggest that the majority of the V_O's are bound to the Co^{2+} dopant ions after

annealing, and unlike unbound vacancies [1,2], the Co_{Ti}^{2+}-V_O complexes do not provide free carriers.

Models of ferromagnetism in a true DMS such as Mn:GaAs rely either on the RKKY-type indirect exchange interactions [10] based on sp-d exchange between transition metal states and free carriers, or the percolation of bound magnetic polarons (BMPs) just below and at the metal-insulator transition [26]. The carrier mediated RKKY-type model does not seem applicable to our highly dielectric Co:TiO$_2$ films where the V_O's are localized to defect sites, and there are presumably no carriers in the valence or conduction bands. Coey *et al.* [27] have proposed a model of indirect exchange for dilute ferromagnetic oxides where shallow donor electrons form BMPs that create a spin-split impurity band. Another mechanism to consider is that of d-d double exchange mediated by tunneling of the d electrons within the impurity band [28]. In band structure calculations for anatase Co:TiO$_2$ [29], the substitutional Co impurities give narrow bands in the forbidden gap, split due to the crystal field into t_{2g} and e_g states. These states are further exchange split, providing conditions for double exchange analogous to doped manganites [13]. When there are V_O's in the system adjacent to the Co ions, the t_{2g} bands split further and the Fermi level appears in the gap, resulting in a *dielectric* ground state. As seen in our experiment, this state is ferromagnetic. Further theoretical study of anatase Co:TiO$_2$ must take into account the observation that free charge carriers are not required for magnetic ordering.

In conclusion, we have provided experimental evidence for intrinsic room temperature ferromagnetism in insulating Co doped anatase TiO$_2$. Highly crystalline, epitaxial anatase Co:TiO$_2$ films were grown by sputter deposition with incorporation of 2 at.% Co into the TiO$_2$ lattice as Co^{2+}. The combination of film growth by sputter deposition and UHV annealing at $450\,^\circ$C prove to be key in avoiding phase segregation and enhancing the ferromagnetic properties of Co:TiO$_2$, which coexist with the dielectric state.

*Author to whom correspondence should be addressed.
Email: kannanmk@u.washington.edu

[1] Y. Matsumoto *et al.*, Science **291**, 854 (2001).

[2] S. A. Chambers *et al.*, Appl. Phys. Lett. **79**, 3467 (2001).

[3] J.-Y. Kim *et al.*, Phys. Rev. Lett. **90**, 017401 (2003).

[4] S. R. Shinde *et al.*, Phys. Rev. Lett. **92**, 166601 (2004).

[5] S. R. Shinde *et al.*, Phys. Rev. B **67**, 115211 (2003).

[6] A. Punnoose, M. S. Seehra, W. K. Park, and J. S. Moodera, J. Appl. Phys. **93**, 7867 (2003).

[7] S. A. Chambers, S. M. Heald, and T. Droubay, Phys. Rev. B **67**, 100401(R) (2003).

[8] T. Dietl, Nat. Mater. **2**, 646 (2003).

[9] J. K. Furdyna, J. Appl. Phys. **64**, R29 (1988).

[10] T. Dietl, H. Ohno, F. Matsukura, J. Cibert, and D. Ferrand, Science **287**, 1019 (2000).

[11] S. A. Wolf *et al.*, Science **294**, 1488 (2001).

[12] H. Saito, V. Zayets, S. Yamagata, and K. Ando, Phys. Rev. Lett. **90**, 207202 (2003).

[13] A. J. Millis, P. B. Littlewood, and B. I. Shraiman, Phys. Rev. Lett. **74**, 5144 (1995); A. J. Millis, Nature (London) **392**, 147 (1998).

[14] S. G. Yang *et al.*, Appl. Phys. Lett. **83**, 3746 (2003).

[15] T. Fukumura *et al.*, Appl. Phys. Lett. **75**, 3366 (1999).

[16] S. Kuwabara *et al.*, Jpn. J. Appl. Phys., Part 2 **40**, L724 (2001); M. L. Reed *et al.*, Appl. Phys. Lett. **79**, 3473 (2001).

[17] N. Theodoropoulou *et al.*, Phys. Rev. Lett. **89**, 107203 (2002).

[18] S. G. Yang, A. B. Pakhomov, S. T. Hung, and C. Y. Wong, Appl. Phys. Lett. **81**, 2418 (2002); Y. Wu *et al.*, Appl. Phys. Lett. **82**, 3047 (2003).

[19] S. B. Ogale *et al.*, Phys. Rev. Lett. **91**, 077205 (2003); J. M. D. Coey, A. P. Douvalis, C. B. Fitzgerald, and M. Venkatesan, Appl. Phys. Lett. **84**, 1332 (2004).

[20] S. A. Chambers *et al.*, Thin Solid Films **418**, 197 (2002).

[21] S. Kraft, J. Stumpel, P. Becker, and U. Kuetgens, Rev. Sci. Instrum. **67**, 681 (1996).

[22] M. Varela, K. A. Griffin, S. Pennycook, and Kannan M. Krishnan (to be published).

[23] RBS measurements courtesy of V. Shutthanandan, Pacific Northwest National Laboratory, Richland, WA.

[24] S. A. Chambers and R. F. C. Farrow, MRS Bull. **28**, 729 (2003).

[25] TRM is useful as a direct measurement of the magnetic signal from the Co:TiO$_2$ film alone because the measurement is taken in zero applied field and there is no contribution from the diamagnetic LAO substrate.

[26] R. N. Bhatt, M. Berciu, M. P. Kennett, and X. Wan, J. Supercond. **15**, 71 (2002); A. Kaminski and S. Das Sarma, Phys. Rev. Lett. **88**, 247202 (2002).

[27] J. M. D. Coey, M. Venkatesan, and C. B. Fitzgerald, Nat. Mater. **4**, 173 (2005).

[28] H. Akai, Phys. Rev. Lett. **81**, 3002 (1998).

[29] M. S. Park, S. K. Kwon, and B. I. Min, Phys. Rev. B **65**, 161201 (2002).