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Influence of a TiO_2 buffer layer on the magnetic properties of anatase Co:TiO_2 thin films

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Our study addresses the influence of a TiO_2 buffer layer on the morphological, structural, and magnetic properties of Co:TiO_2 films grown on (001) $SrTiO_3$ substrates by RF sputtering. We demonstrate that a direct correlation exist between the morphology, the Co heterogeneity, and the magnetic properties measured in the films. Correlated analysis by cross section transmission electron microscopy, energy dispersive x-ray, and x-ray photoemission spectroscopy reveals that the Co is not uniformly distributed in the film but concentrated in the surface clusters. Atomic force microscopy analysis illustrates that the unbuffered films present a large density of surface clusters. These clusters are not metallic Co but Co rich TiO_2 anatase phase and they are accompanied by structural defects in the film: dislocations, small angle grain boundaries. Magnetometry analysis shows that the unbuffered films have a net ferromagnetic behavior, while in the buffered ones the ferromagnetism is quenched. Therefore, we conclude that the magnetism in unbuffered samples is related to the surface clusters and seems to have an extrinsic nature. [http://dx.doi.org/10.1063/1.4706570]

I. INTRODUCTION

Dilute magnetic oxides (DMOs) are semiconducting or insulating oxides that turn ferromagnetic when doped with small amounts of transition metal ions. These materials have attracted a lot of interest due to their potential integration in the field of spintronics.[1] Among the large variety of DMOs, the Co doped TiO_2 was the first to be reported ferromagnetic at room temperature.[2] Since the dopant concentration is usually lower than the percolation threshold, the magnetic behavior of this system cannot be understood in terms of classical theories of magnetism in oxides.[3] The lack of suited theories to explain the experimental observations generated a controversy about the origin of the ferromagnetism. A series of studies indicated an intrinsic origin[4–8] while others suggested an extrinsic one.[9–11] However, the Co:TiO_2 system shows anomalous Hall effect[6,12,13] and magneto-optical dichroism[14–16] typical for ferromagnetic spin polarized carriers, which could lead to practical spintronic applications.

Integrating Co:TiO_2 into a complex spintronic multilayered stack requires the development of thin films with high structural quality and flat surface morphology that should exhibit ferromagnetic properties. In this paper, we study the influence of a TiO_2 buffer layer on the morphological, structural, and magnetic properties of Co:TiO_2 films with grown on (001) $SrTiO_3$ single crystal substrates using conventional RF sputtering deposition technique. We show that a direct correlation exists between the morphological properties, Co heterogeneity, and the magnetic properties of our films.

II. EXPERIMENTAL

The Co:TiO_2 (5 at. %) films were grown on (001) $SrTiO_3$ single crystal substrates by RF sputtering using a sintered target with the same composition which was synthesized by the standard solid-state route. The base pressure in the deposition chamber was better than 5×10^{-8} Torr. The Ar pressure during sputtering was set to 5 mTorr and the oxygen partial pressure to 1×10^{-4} Torr. A RF power density of 6 W/cm^2 was used, that provides, in the case of our specific system, a relative low growth rate of 0.12 nm/min which is considered to promote a layer-by-layer growth mode.[17] The substrate temperature was maintained at 550 °C during growth and after deposition was naturally cooled down to room temperature in 1×10^{-4} Torr of oxygen. The TiO_2 buffer layer was deposited from a stoichiometric ceramic target using the same RF power, Ar and O_2 partial pressures, at a higher substrate temperature of 650 °C. After growth, the buffer layer was annealed at 550 °C for 1 h in 10^{-2} Torr of O_2.

The structural properties of the samples have been analyzed by x-ray diffraction (XRD) using a high resolution four circle diffractometer. The valence states of the films constituents were determined by x-ray photoelectron spectroscopy (XPS). The microstructure was examined in cross section by high resolution transmission electron microscopy (HRTEM). The surface morphology was analyzed by atomic force microscopy (AFM) and the magnetic characteristics were investigated by superconducting quantum interference device (SQUID) magnetometry.

III. RESULTS AND DISCUSSIONS

In order to facilitate the growth of anatase phase TiO_2 films, we used (001) $SrTiO_3$ single crystalline substrates for

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which the lattice mismatch with the anatase phase is 3.1%. Before deposition, we performed a chemical and a heat treatment on the substrate in order to obtain a well ordered TiO_2 terminated surface.[18] The treatment consists of a hydrolysation of the substrate surface in deionized water and a chemical etching in buffered hydrofluoric acid. An annealing process at 950 °C in oxygen atmosphere is performed to trigger a reorganization of the surface. After this treatment, well ordered atomically flat terraces form on the substrate surface as indicated by AFM analysis (Fig. 1).

Two types of films were studied: one deposited directly on the as-prepared substrate and the other grown on a 5 nm thick TiO_2 buffer layer.

Figure 2 shows selected area 2θ-ω x-ray diffraction patterns of 40 nm thick Co:TiO_2 films grown with and without the 5 nm thick TiO_2 buffer layer. The observed peaks correspond only to the (004) reflection of the TiO_2 anatase phase and to the (002) reflection of the $SrTiO_3$ substrate, indicating the epitaxial growth. Within the measurement resolution no signs of other phases or metallic Co clustering were observed. The full width at half maximum of the XRD rocking curves (shown in the inset of Fig. 2) around the (004) reflection for these films is about ~1.2°.

Figure 3 shows AFM images recorded for the buffered and unbuffered Co:TiO_2 layers. A net discrepancy between the two types of films can be observed. While both films show a flat surface morphology, the unbuffered one presents a relative large density of surface particulates. The different morphologies can be explained if one takes into account that due to the in-plane lattice mismatch a relative large misfit strain is expected at the anatase/$SrTiO_3$ interface, which gives rise to structural defects (dislocations, small angle grain boundaries, etc.). The defects represent high mobility channels for the diffusion of Co which will eventually cluster on the surface. However, by the insertion of the TiO_2 buffer layer, the density of defects in the Co doped film is strongly reduced, thus reducing the density of surface clusters.

Figure 4 shows SQUID measurements recorded at 5 K for unbuffered, buffered Co:TiO_2 films, and on the bare $SrTiO_3$ substrate. As one can observe, the buffering of the Co:TiO_2 films has a dramatic effect on the magnetic properties. The unbuffered film shows a clear ferromagnetic hysteresis loop (Fig. 4(a)), while the magnetic signal is strongly reduced in the case of the buffered film, being undistinguishable from the one of the substrate (Fig. 4(b)). The small *parasitic* magnetic signal observed for the bare substrate is

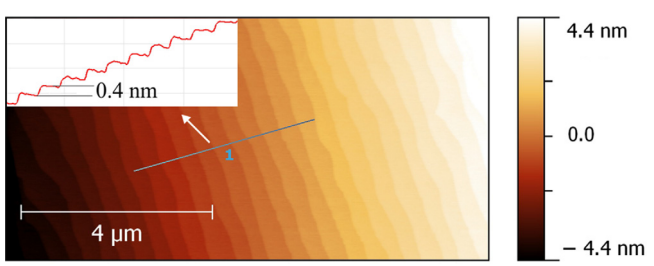

FIG. 1. AFM image of the $SrTiO_3$ substrate surface after the chemical treatment and annealing, showing the formation of large, atomic flat, well regulated terraces. The inset shows a height profile corresponding to the indicated line.

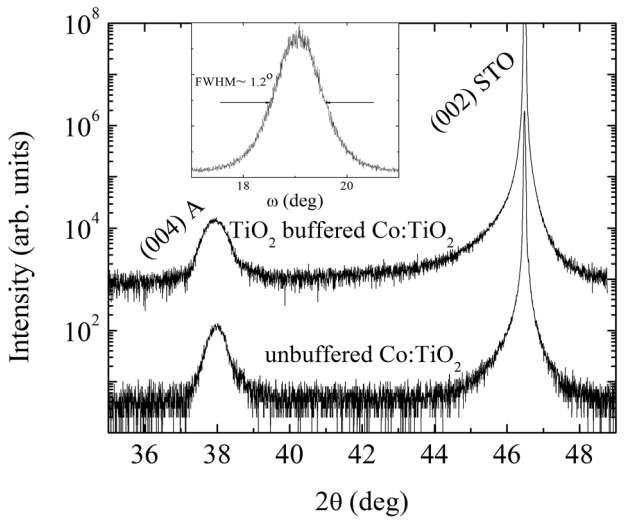

FIG. 2. 2θ-ω x-ray diffraction selected area scans of 40 nm thick Co:TiO_2 films with and without the 5 nm thick TiO_2 layer. The scans were shifted vertically for better visibility. The inset shows the XRD rocking curve for the buffered film.

most likely due to some contamination during the substrate manufacturing process.[19] These results stress out the strong influence of the surface clusters on the magnetic properties of our Co:TiO_2 films.

In order to investigate the valence states of the films constituents we preformed XPS studies. XPS is a surface sensitive technique which, in principle, should allow us to identify the nature of the surface clusters. Figure 5 shows the Ti and Co 2p core level spectra of the unbuffered Co:TiO_2 film. The core level binding energies of Ti $2p_{1/2}$ and Ti $2p_{3/2}$ are 465.2 eV and 459.5 eV, respectively, and match well with standard binding energies of Ti^{4+} in anatase phase structure.[20] The line separation between Ti $2p_{1/2}$ and Ti $2p_{3/2}$ is 5.7 eV, consistent with the standard binding energy. The core level binding energies of Co $2p_{1/2}$ and Co $2p_{3/2}$ are 796.5 eV and 781.1 eV, respectively, with separation of

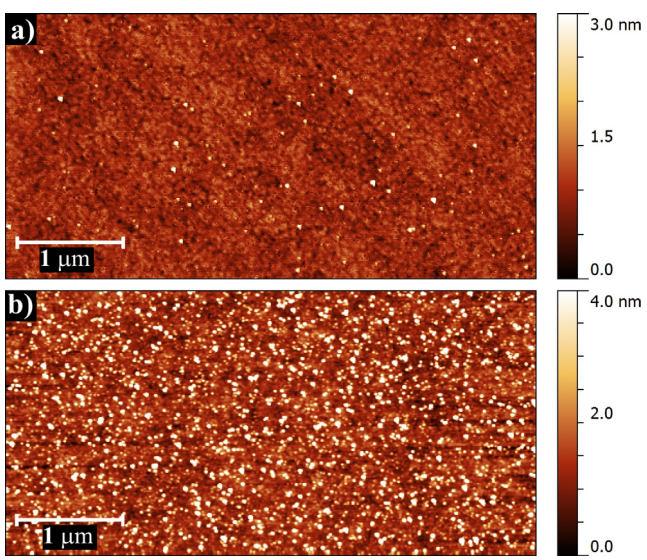

FIG. 3. AFM images of Co:TiO_2 films grown grown (a) with and (b) without the TiO_2 buffer layer.

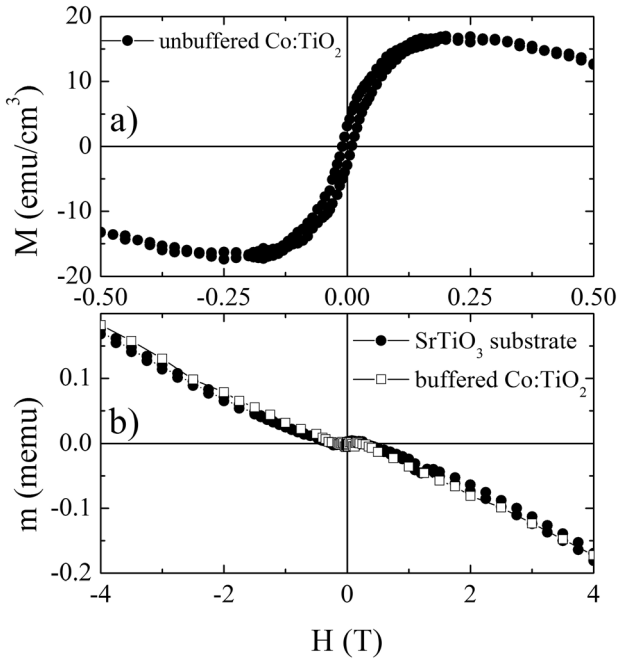

FIG. 4. Magnetic hysteresis loops performed at 5 K for the (a) unbuffered and (b) buffered $Co:TiO_2$ films and on the bare $SrTiO_3$ substrate.

15.4 eV between the two lines. The satellite peaks on the high energy binding side of Co $2p_{1/2}$ and Co $2p_{3/2}$ lines reveal the existence of Co^{2+} in a high spin state.[21] These measurements are an indication that Co does not precipitate as metallic Co on the film surface, since then the Co $2p_{3/2}$ will be expected at much lower energies (778.5 eV).[22]

To investigate the Co distribution into the TiO_2 matrix we employed cross-sectional TEM analysis. Figure 6 shows a cross-sectional bright field image of the $Co:TiO_2$ unbuffered film. The image clearly indicates the presence of clusters on the film surface, in agreement with the AFM analysis. The inset of the figure shows a high resolution TEM image of the emphasized region containing surface clusters. A careful examination shows that the presence of clusters is accompanied by structural defects such as dislocations, small angle grain boundaries, etc. Moreover, it seems that the clusters are crystalline and nucleate on top of the continuous epitaxial film. The clusters have the same orientation as the epitaxial film and interplanar spacing measurements indicate that are still in the anatase phase.

In order to investigate the nature of the clusters, we performed energy dispersive x-ray analysis (EDX). Figure 7 shows EDX elemental mapping of a film area containing a cluster. Interestingly, the elemental mappings show that Co is not uniformly distributed throughout the film but concentrated in the surface cluster and in the region beneath it. This suggests that, indeed, Co diffuses through defects and form Co rich anatase regions. Outside these regions, within the limits of the measurements accuracy, the Co concentration is negligible (the Co signal coming from the areas outside the Co rich regions is practically similar to the one coming from the substrate, for which no Co should be present). Nevertheless, we cannot completely rule out the possibility of some Co to be uniformly distributed throughout the anatase lattice due to the finite detection limit of the EDX measurement. However, we clearly show that in our film the Co is mostly segregated into certain Co rich regions that extend beneath the surface clusters. Moreover, as also indicated by the XPS measurements (Fig. 5), the Co rich regions are not Co metallic clusters but Co rich anatase regions. The formation of Co

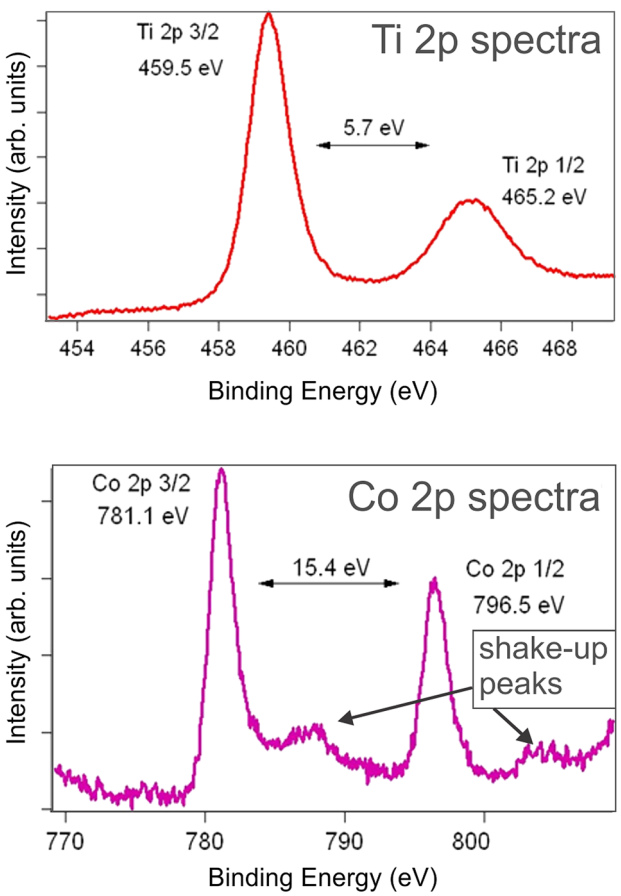

FIG. 5. The Ti and Co 2p XPS spectra for the unbuffered $Co:TiO_2$ film.

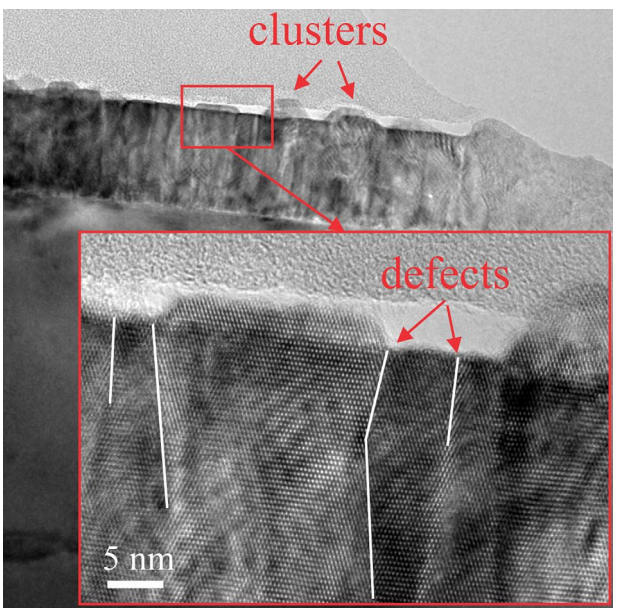

FIG. 6. Cross-sectional bright field image of the $Co:TiO_2$ unbuffered film. Inset shows a high resolution TEM image of the emphasized region containing surface clusters.

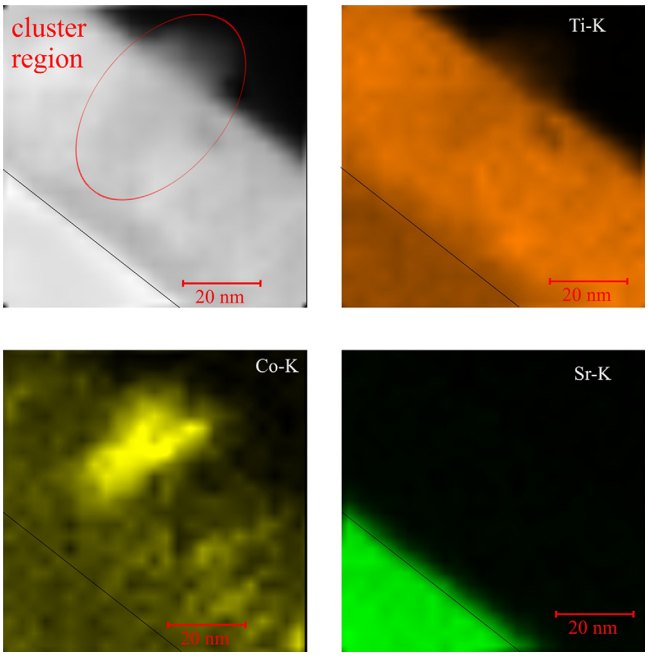

FIG. 7. EDX elemental mappings of a region in the unbuffered Co:TiO_2 film containing surface clusters.

rich anatase clusters is supported by density functional theory calculations,[23] which show that non-uniform doping mode with short Co-Co distances is energetically more favorable over the uniform distribution of Co throughout the lattice. Although, we cannot definitely say that the ferromagnetic signal of our films is only due to this Co rich regions, certainly, as indicated by the SQUID measurements (see Fig. 4) they have a strong impact on the ferromagnetic properties of our films. Quantifying the strength of magnetization of these Co rich regions will require estimating the volume of the clusters with respect to the total volume of the film. Unfortunately, TEM bright field images over large areas do not allow clear and sufficiently accurate identification of the clusters volume extension. On the other hand, the HRTEM analysis gives better local information about the clusters volume, but with a bad statistics due to their limited area. Therefore, this type of analysis would lead to a large uncertainty of the estimated clusters-film volume fraction and consequently of the clusters magnetization.

In conclusion, we showed, in the case of unbuffered Co:TiO_2 films, the presence of a large density of surface clusters which consists of Co enriched anatase phase. The Co concentration outside these regions is negligible. If a TiO_2 buffer layer is used, as confirmed by the AFM analysis, the density of surface clusters is drastically reduced. The clusters have a strong influence on the magnetic properties of our films. The unbuffered film shows a clear ferromagnetic hysteresis loop, while the magnetic signal is undistinguishable from the one of the substrate in the case of the buffered ones. Our results are in agreement with those reported for doped TiO_2 films grown by molecular beam epitaxy, for which it was shown that in the case of ferromagnetic films the dopants tend to segregate into nanoscale clusters. On the other hand, homogenous films were found to be non-ferromagnetic.[10,24,25] Recently,[26] it was pointed out that the insertion of a TiO_2 buffer layer in pulse laser deposited Co:TiO_2 films leads to a reduction of the density of Co clusters and the suppression of the anomalous Hall effect which was thought to be induced by clusters. These findings suggest an extrinsic nature of ferromagnetism and seem to indicate a limited applicability in the field of spintronics, especially since uniform doped films tend to be non-ferromagnetic and the development of cluster based films with tunable and reproducible ferromagnetic properties is an extremely difficult task.

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[1]S. A. Wolf, D. D. Awschalom, R. A. Buhrman, J. M. Daughton, S. von Molnar, M. L. Roukes, A. Y. Chtchelkanova, and D. M. Treger, Science **294**, 1488–1495 (2001).
[2]Y. Matsumoto, M. Murakami, T. Shono, T. Hasegawa, T. Fukumura, M. Kawasaki, P. Ahmet, T. Chikyow, S.-Y. Koshihara, and H. Koinuma, Science **291**, 854–856 (2001).
[3]J. Coey, Curr. Opin. Solid State Mater. Sci. **10**, 83–92 (2006).
[4]K. A. Griffin, A. B. Pakhomov, C. M. Wang, S. M. Heald, and K. M. Krishnan, Phys. Rev. Lett. **94**, 157204 (2005).
[5]J. W. Quilty, A. Shibata, J.-Y. Son, K. Takubo, T. Mizokawa, H. Toyosaki, T. Fukumura, and M. Kawasaki, Phys. Rev. Lett. **96**, 027202 (2006).
[6]H. Toyosaki, T. Fukumura, Y. Yamada, K. Nakajima, T. Chikyow, T. Hasegawa, H. Koinuma, and M. Kawasaki, Nature Mater. **3**, 221 (2004).
[7]Y. Yamada, H. Toyosaki, A. Tsukazaki, T. Fukumura, K. Tamura, Y. Segawa, K. Nakajima, T. Aoyama, T. Chikyow, T. Hasegawa, H. Koinuma, and M. Kawasaki, J. Appl. Phys. **96**, 5097–5102 (2004).
[8]H. Toyosaki, T. Fukumura, Y. Yamada, and M. Kawasaki, Appl. Phys. Lett. **86**, 182503 (2005).
[9]S. R. Shinde, S. B. Ogale, J. S. Higgins, H. Zheng, A. J. Millis, V. N. Kulkarni, R. Ramesh, R. L. Greene, and T. Venkatesan, Phys. Rev. Lett. **92**, 166601 (2004).
[10]S. A. Chambers, T. Droubay, C. M. Wang, A. S. Lea, R. F. C. Farrow, L. Folks, V. Deline, and S. Anders, Appl. Phys. Lett. **82**, 1257–1259 (2003).
[11]J.-Y. Kim, J.-H. Park, B.-G. Park, H.-J. Noh, S.-J. Oh, J. S. Yang, D.-H. Kim, S. D. Bu, T.-W. Noh, H.-J. Lin, H.-H. Hsieh, and C. T. Chen, Phys. Rev. Lett. **90**, 017401 (2003).
[12]K. Ueno, T. Fukumura, H. Toyosaki, M. Nakano, and M. Kawasaki, Appl. Phys. Lett. **90**, 072103 (2007).
[13]R. Ramaneti, J. C. Lodder, and R. Jansen, Appl. Phys. Lett. **91**, 012502 (2007).
[14]H. Toyosaki, T. Fukumura, Y. Yamada, and M. Kawasaki, Appl. Phys. Lett. **86**, 182503 (2005).
[15]T. Yamasaki, T. Fukumura, Y. Yamada, M. Nakano, K. Ueno, T. Makino, and M. Kawasaki, Appl. Phys. Lett. **94**, 102515 (2009).
[16]Y. Hirose, T. Hitosugi, Y. Furubayashi, G. Kinoda, K. Inaba, T. Shimada, and T. Hasegawa, Appl. Phys. Lett. **88**, 252508 (2006).
[17]S. Chambers, C. Wang, S. Thevuthasan, T. Droubay, D. McCready, A. Lea, V. Shutthanandan, and C. F. Windisch, Jr., Thin Solid Films **418**, 197–210 (2002).
[18]M. Kawasaki, K. Takahashi, T. Maeda, R. Tsuchiya, M. Shinohara, O. Ishiyama, T. Yonezawa, M. Yoshimoto, and H. Koinuma, Science **266**, 1540–1542 (1994).
[19]S. M. M. Yee, D. A. Crandles, and L. V. Goncharova, J. Appl. Phys. **110**, 033906 (2011).
[20]*Handbook of X-Ray Photoelectron Spectroscopy*, edited by G. E. Muilenberg (Perkin-Elmer, Eden Prairie, 1979).
[21]B.-S. Jeong, Y. W. Heo, D. P. Norton, J. G. Kelly, R. Rairigh, A. F. Hebard, J. D. Budai, and Y. D. Park, Appl. Phys. Lett. **84**, 2608–2610 (2004).

[22]J. Chai, J. Pan, S. Wang, C. Huan, G. Lau, Y. Zheng, and S. Xu, Surf. Sci. **589**, 32–41 (2005).
[23]Z. Yang, G. Liu, and R. Wu, Phys. Rev. B **67**, 060402 (2003).
[24]T. C. Kaspar, T. Droubay, D. E. McCready, P. Nachimuthu, S. M. Heald, C. M. Wang, A. S. Lea, V. Shutthanandan, S. A. Chambers, and M. F. Toney, J. Vac. Sci. Technol. B **24**, 2012–2017 (2006).
[25]T. C. Kaspar, T. Droubay, V. Shutthanandan, S. M. Heald, C. M. Wang, D. E. McCready, S. Thevuthasan, J. D. Bryan, D. R. Gamelin, A. J. Kellock, M. F. Toney, X. Hong, C. H. Ahn, and S. A. Chambers, Phys. Rev. B **73**, 155327 (2006).
[26]Y. J. Lee, M. P. de Jong, W. G. van der Wiel, Y. Kim, and J. D. Brock, Appl. Phys. Lett. **97**, 212506 (2010).