Anomalous Hall effect suppression in anatase Co:TiO₂ by the insertion of an interfacial TiO₂ buffer layer

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We present the effect of introducing a TiO₂ buffer layer at the SrTiO₃/Co:TiO₂ interface on the magnetic and structural properties of anatase Co:TiO₂ (1.4 at. % Co). Inserting the buffer layer leads to suppression of the room-temperature anomalous Hall effect, accompanied by a reduced density of Co clusters, and a different depth distribution of such clusters. Co clusters in Co:TiO₂ with a buffer layer are mostly formed at the surface, such that they are situated outside the current path and cannot contribute to the transverse anomalous Hall resistivity. These results indicate extrinsic origins of magnetism in anatase Co:TiO₂. © 2010 American Institute of Physics. [doi:10.1063/1.3521286]

Dilute magnetic semiconductors (DMSs) are uniquely characterized by carrier-mediated magnetism, i.e., ferromagnetism and carrier spin polarization controlled by the carrier density via doping or electrical gating, a highly interesting attribute for spintronic applications. One of the well-known characteristics of DMSs is the anomalous Hall effect (AHE).^{1,2} AHE measurements in a field-effect transistor configuration have played a crucial role in confirming carrier-mediated magnetism in (Ga,Mn)As and (In,Mn)As systems by showing electrical control of the Curie temperature T_C (Ref. 1) and magnetization direction.² Recently, following theoretical predictions by Dietl,³ wide band gap oxides and nitrides have been extensively studied as candidate systems for room-temperature DMSs. In particular, Co doped TiO₂ (Co:TiO₂) is one of the most widely studied materials that have been reported to show room-temperature ferromagnetism,⁴ magneto-optical dichroism,^{5,6} and the AHE in rutile, anatase, and even amorphous phases.⁷⁻¹⁰

However, the origin of ferromagnetism in Co:TiO₂ remains controversial. Numerous partially conflicting observations have been reported that point toward both intrinsic and extrinsic origins. The controversy persists partially due to the fact that the presence of a small amount of heterogeneity in otherwise homogeneous samples may escape detection by (in-house) structural characterization methods such as x-ray diffraction (XRD) and high-resolution transmission electron microscopy. The observation of ferromagnetic signals using standard, macroscopic magnetometry techniques in such samples can therefore not be taken as unambiguous proof of intrinsic carrier-mediated magnetism. Furthermore, even the presence of the AHE cannot be considered as a definite test for intrinsic DMS behavior, since it has been shown that the AHE can be observed also in the presence of Co clusters.¹¹

Here, we study the effect of inserting a TiO₂ buffer layer at the SrTiO₃(STO)/Co:TiO₂ interface on the magnetic and structural properties of anatase Co:TiO₂ with complementary techniques such as AHE measurements, vibrating sample magnetometry (VSM), XRD, and energy-filtered transmission electron microscopy (EFTEM). Since the Co

distribution is heterogeneous for Co:TiO₂ films grown on STO under oxygen poor conditions,¹² a TiO₂ buffer layer is introduced in order to increase the homogeneity of Co. Furthermore, we will investigate the validity of the employment of AHE measurements for the verification of carrier-mediated magnetism.

Epitaxial thin films of anatase Co:TiO₂ (1.4 at. %) with/without TiO₂ buffer layer (20 nm, 10⁻³ mbar, 550 °C) were grown by pulsed laser deposition on TiO₂-terminated (100) STO substrates under oxygen poor (9 × 10⁻⁵ mbar) conditions. More details on growth, transport, and magnetic properties were presented previously.⁹ X-ray diffraction, using a high-resolution four circle x-ray diffractometer, was carried out to investigate the structural properties of 165 nm thick Co:TiO₂ films, with/without buffer layer, and to check for Co heterogeneity. EFTEM measurements were performed on 165 nm thick Co:TiO₂ films with/without buffer layer.

Figure 1 shows θ -2 θ x-ray diffraction spectra measured on 165 nm thick Co:TiO₂ films without and with buffer layer, respectively. Since a θ -2 θ scan investigates only out-of-plane Bragg points in reciprocal space, it may not be a robust characterization method to detect otherwise offset

FIG. 1. θ -2 θ x-ray diffraction spectra of Co:TiO₂ films (a) without and (b) with buffer layer. The inset in (a) shows an offset θ -2 θ scan.

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FIG. 2. AFM images of Co:TiO₂ films (a) without and (b) with buffer layer.

grown Co clusters (different *c*-axis orientation). However, clear evidence for the presence of Co metal clusters is nevertheless detected in case of the Co:TiO₂ film without buffer layer [Fig. 1(a)]. Even offset θ -2 θ scans [inset of Fig. 1(a)] also reveal Co peaks, providing evidence for randomly oriented Co clusters. It should be noted that the AHE measurements in Ref. 9 were carried out for films thicker than 160 nm (550 nm, 185 nm), also grown without buffer layer. This means that the AHE reported in that study occurs in the presence of Co clusters.

Figures 2 and 3 show images obtained from atomic force microscopy (AFM) and EFTEM measurements, respectively. The insertion of the buffer layer results in clear differences concerning the formation and distribution of Co clusters in the thin film. Figure 2(b) shows that a significantly reduced areal density of rutile outgrowths is present on Co:TiO₂ thin films when the buffer layer is inserted. In Fig. 3, EFTEM analysis reveals that Co clustering is accompanied by the formation of rutile outgrowths, which emanate from the Co clusters and protrude significantly from the surface. For films without buffer layer [see Figs. 3(a) and 3(b)], the Co clusters are located at the film/substrate interface, while they appear close to the surface [see Figs. 3(c) and 3(d)] if a buffer layer is included. From this observation we conclude that the buffer layer plays a prominent role in reducing the amount of defects at the interface, such as dislocations and grain boundaries, which are favored nucleation sites of Co clusters and the accompanying rutile outgrowths. It is worth noting that Co clusters are still observed in Co:TiO₂ thin films with buffer layer by EFTEM measurements, but not by XRD. This shows that care must be taken when using (in-house) XRD for the confirmation of structural homogeneity, since a small number of tiny metallic clusters in the thin film may not be detected.

Figure 4 shows VSM measurements and AHE resistivities for 165 nm thick Co:TiO₂ films with and without buffer

FIG. 3. EFTEM images of Co:TiO₂ films [(a) and (b)] without and [(c) and (d)] with buffer layer. [(a) and (c)] Images represent Co maps (in white), while (b) and (d) are Ti maps (in white).

FIG. 4. (a) Magnetic moment vs out-of-plane field for Co:TiO₂ films with (squares) and without (circles) buffer layer at room temperature. (b) Anomalous Hall resistivity for Co:TiO₂ films with (squares) and without (circles) buffer layer.

layers. The latter have been obtained by subtracting the linear ordinary Hall contribution from Hall measurements. The Hall resistivity ρ_{xy} in ferromagnets is expressed empirically as a sum of ordinary and anomalous terms, $\rho_{xy} = R_0 B + \mu_0 R_s M$. The first term is the ordinary Hall contribution where R_0 is the ordinary Hall coefficient, and B is the magnetic flux density. It is related to the deflected motion of carriers due to the Lorentz force. The second term is the anomalous term, proportional to the perpendicular component of the magnetization (M) in the ferromagnet (R_s : the anomalous Hall coefficient, μ_0 : permeability in vacuum). The carrier concentrations for Co:TiO₂ films with and without buffer layers at room temperature are 8.6×10^{18} and $2.3 \times 10^{19}/\text{cm}^3$, respectively.

The most striking finding is that for the Co:TiO₂ thin film with buffer layer, the hysteresis shape of the AHE and magnetization (VSM) measurements is completely different (see Fig. 4): the anomalous Hall effect is strongly (if not completely) suppressed, while the VSM measurement still shows a ferromagnetic hysteresis loop. In contrast, the ρ_{AHE} for the Co:TiO₂ thin film without buffer layer shows only a slightly different hysteresis loop shape compared to that of the perpendicular magnetization. The suppressed AHE in Co:TiO₂ films with buffer layer can be explained by the fact that the insertion of the buffer layer reduces the overall density of Co clusters, prevents the nucleation of such clusters at the STO/Co:TiO₂ interface, and instead leads to the formation of Co clusters above a certain critical thickness. The repeatedly formed Co clusters at the interface in Co:TiO₂ films without buffer layers may induce spin polarization by extrinsic (i.e., induced by the clusters) spin orbit scattering, and thus give rise to a transverse anomalous Hall resistivity. In contrast, the AHE in Co:TiO₂ films with buffer layers is suppressed by (1) the reduction of Co clusters and (2) the

formation of the Co clusters above a critical thickness, such that they always appear close to the surface of the film, often even inside the rutile outgrowths. From Figs. 3(c) and 3(d), it is evident that Co clusters formed in the rutile outgrowths, protruding outside the surface, cannot contribute to the transverse anomalous Hall resistivity, since these clusters are not located within the path of the current that flows through the Co:TiO₂ during the measurement.

One might argue that carrier-mediated magnetism cannot be ruled out as a mechanism for the suppression of the AHE, since the twice or three times smaller carrier concentration for Co:TiO₂ films with buffer layers may reduce the ferromagnetic exchange interaction and thus the AHE signal. However, the insertion of the buffer layers produces more isolated Co²⁺ magnetic moments in the thin film, since less Co goes into clusters, as can be seen from XRD and EFTEM results. Therefore, a suppression of the ferromagnetic exchange interaction by a reduction of the carrier concentration is not expected.

It is also worth investigating the scaling relation in the observed AHE conductivity σ_{xy}^{AH} of Co:TiO₂ films, $\sigma_{xy}^{AH} \propto \sigma_{xx}^\alpha$, where σ_{xx} is the longitudinal conductivity, since the scaling exponent α is related to the origin of the AHE.¹³ For low-conductivity materials, α is predicted to be 1.6.¹⁴ The 1.6 scaling exponent was found experimentally in rutile Co:TiO₂,¹⁵ (Ga,Mn)As,¹³ and magnetic oxides.¹⁶ In intrinsic DMSs, a wide range of conductivities can be obtained by changing the temperature or the doping concentration in order to determine the scaling exponent. However, it is difficult to obtain a distinct scaling exponent in anatase Co:TiO₂, since the conductivity does not change much within the whole temperature range studied. In particular, the AHE in anatase Co:TiO₂ without buffer layer is observed within the whole temperature range. Moreover, the anomalous Hall resistivity is nearly independent of temperature.

The observation of the AHE in the presence of metallic clusters in Co:TiO₂ thin films is consistent with the previous report by Shinde *et al.*¹¹ Here, however, by the insertion of a buffer layer, we also show that the AHE disappears when the density of Co clusters is reduced, and, perhaps more importantly, the Co clusters form above a critical thickness instead of at the substrate/film interface. Due to the latter, many of the clusters reside close to the surface and even inside the rutile outgrowths, such that they fall outside of the current path and thus cannot contribute significantly to the AHE. These results confirm that the presence of AHE itself does not imply intrinsic, i.e., carrier-mediated, magnetism in DMS research. Zhang¹⁷ pointed out that the AHE originating from extrinsic metallic clusters is featured by a very small value of the ratio of the anomalous Hall resistivity to the longitudinal resistivity ($\rho_{AHE}/\rho_{xx} \sim 10^{-4}$) compared to that (10^{-2}) ob-

served in intrinsic DMSs. Co:TiO₂ films without buffer layers indeed show similar very small values of ρ_{AHE}/ρ_{xx} , about 10^{-4} , again indicating the extrinsic origin of the AHE, i.e., due to metallic clusters.

To summarize, the AHE in Co:TiO₂ films without buffer layer can be explained well by Co clusters formed at the substrate/film interface, which give rise to an anomalous transverse Hall resistivity by polarizing nearby electrons. The clearest evidence for a cluster-induced AHE is, however, the observation that the AHE is strongly (if not completely) suppressed for Co:TiO₂ films with buffer layer, in which the Co clusters are reduced in density and preferentially located at the surface.

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