Anomalous Hall effect in anatase Co:TiO₂ ferromagnetic semiconductor

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The observation of the anomalous Hall effect (AHE) in Co-doped TiO₂ ferromagnetic semiconductor in the anatase phase is reported. An AHE is observed with magnetic hysteresis consistent with remanence and coercivity obtained from magnetometry data. The anatase films also have reasonable mobility (~17 cm²/V·s) at room temperature and carrier density of ~5 × 10¹⁸ cm⁻³. The AHE in such films with relatively low carrier density gives prospects to test whether the ferromagnetism in this oxide semiconductor is carrier mediated using a field effect device configuration. © 2007 American Institute of Physics. [DOI: 10.1063/1.2751133]

Ferromagnetism mediated by charge carriers in dilute magnetic semiconductors (DMSs) creates materials with unique functionality for application in spintronic devices.¹² Electrical control of ferromagnetism in III-V based DMS (Refs. 3 and 4) has provided conclusive evidence that delocalized carriers (holes) mediate the magnetic exchange interaction between the dilute concentrations of localized moments, thus producing a macroscopic magnetization. By manipulating the carrier density of the semiconductor in a field effect transistor (FET) configuration, changes could be induced in the Curie temperature and other magnetic properties such as the coercivity.³⁴ These were monitored using the anomalous Hall effect (AHE),³⁶ which has historically been an important tool to study magnetization processes in ferromagnetic materials.

A similar approach may be envisioned to establish the origin of ferromagnetism and the role of the charge carriers in other DMS.⁷ An attractive class of materials are the doped oxide semiconductors, for which ferromagnetic order persists to higher temperature, well above room temperature.⁸–¹⁰ However, the origin of the ferromagnetism in DMS oxides is still controversial. In order to be able to perform a decisive test using a FET device structure, it is a prerequisite that the material shows a measurable AHE and at sufficiently low carrier density to enable electrical gating. The AHE has been reported in rutile Co:TiO₂ DMS,¹¹–¹³ but the high carrier density (10²⁰–10²² cm⁻³) precludes electric field control. On the other hand, the observation of the AHE in the case of Co:TiO₂ in the anatase phase is rare.¹⁴,¹⁵

In this letter we report on the observation of the AHE in anatase Co₉Ti₁₋₉O₂ (x=0.014) at relatively low carrier density. Thin Co:TiO₂ films were grown by pulsed laser deposition on TiO₂ terminated (100) SrTiO₃ substrates. Ablation of a Co₉Ti₁₋₉O₂ (x=0.014) target was carried out using a KrF excimer (λ=248 nm) laser with a fluence of 1.8 J/cm² at a rate of 5 Hz. The temperature during growth of the films was fixed at 550 °C while the oxygen pressure (Pₒ₂) was maintained at 7×10⁻⁵ mbar. Supplementary structural analysis was obtained from x-ray diffraction (XRD) and transmission electron microscopy (TEM). Magnetization was measured in a vibrating sample magnetometer (VSM) at 300 K on 5×10 mm² samples. Electrical transport including Hall measurements was carried out in the temperature range from 5 to 300 K using a four terminal van der Pauw configuration in magnetic fields up to 1 T.

The Hall resistivity is commonly expressed as ρₓᵧ = Rₒ B + μ₀ Rₓ Mₓᵧ. It comprises the ordinary Hall effect (OHE) term (Rₒ B=1/ne), where Rₒ is the ordinary Hall coefficient, B is the magnetic induction, and n is the carrier density of the semiconductor. The AHE term is proportional to the perpendicular component of magnetization (Mₓᵧ), the anomalous Hall coefficient (Rₓ), and the permeability in vacuum (μ₀). Initial measurements were made on a 550 nm Co:TiO₂ thin film at room temperature. The bottom panel of Fig. 1

FIG. 1. Top panel: Anomalous Hall resistivity vs the out-of-plane applied magnetic field for a 550 nm Co:TiO₂ thin film. The data are obtained from the total Hall resistivity shown in the inset by subtracting the linear term due to the OHE. The inset has the same units as the main panel. Bottom panel: Magnetization with the field applied in plane (open circles) and out of plane (solid circles) of the same sample. All measurements were done at room temperature.

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shows the room temperature magnetization measured by VSM with the field applied in plane and perpendicular to the film plane. The film shows a slight perpendicular anisotropy with a saturation magnetization of 10 kA/m, a coercivity of 360 Oe, and a remanence of 5 kA/m. Hall measurements on the same sample show that at sufficiently high magnetic fields the Hall resistivity is linear with a negative slope, corresponding to a \( n \)-type semiconductor with a carrier density of \( \sim 3 \times 10^{18} \) cm\(^{-3} \). At fields close to zero a small nonlinear signal is observed. By subtracting the linear OHE term a clear signature is obtained corresponding to the AHE. This is shown in the top panel of Fig. 1 where the anomalous Hall resistivity \( \rho_{\text{AHE}} \) is plotted against the applied magnetic field. The nonlinearity in the \( \rho_{\text{AHE}} \) signal shows up as a hysteresis, with a nonzero signal at zero field, and the signal reaching saturation of opposite sign at high positive, respectively, negative fields. The shape of the AHE curve is consistent with the out-of-plane magnetization curve, including the remanence and coercivity values, as expected for the AHE being proportional to \( M_z \).

Structural analysis of this sample by XRD and cross-sectional TEM indicated the presence of a mixed phase comprising some rutile phase in the surface region. Since the AHE has been observed for rutile Co:TiO\(_2\), the AHE data of Fig. 1 could not be attributed unambiguously to the anatase phase. However, the observation of AHE in a mixed phase sample is consistent with the similar AHE we observe in pure anatase Co:TiO\(_2\) films grown under the same conditions, as described below. It was found that for films of less than 200 nm, XRD spectra show only (004) and (008) reflections corresponding to pure anatase TiO\(_2\). Subsequently, thin films of less than 200 nm that are pure anatase were studied.

Results from cross-sectional TEM of a 75 nm Co:TiO\(_2\) film are shown in Fig. 2. The film is well ordered and epitaxial but has a mosaic spread with low angle grain boundaries (indicated by arrows in the middle panel). This results in moiré fringes (top panel) and strain patterns visible at lower magnification (middle panel). Higher resolution images taken near the interface (bottom panel) as well as selective area electron diffraction (SAED) confirm that the films up to about 200 nm thickness are in the anatase phase, with out-of-plane lattice parameter \( c = 9.51 \) Å and in-plane lattice parameter \( a = 3.79 \) Å. These values are in agreement with the bulk values for anatase TiO\(_2\). The in-plane parameter is 3% smaller than the in-plane lattice parameter (3.905 Å) of the SrTiO\(_3\) (100) substrate. The lattice mismatch results in significant defect density at the interface between the film and substrate (bottom panel).

Hall transport measurements were carried out on 185 nm pure anatase Co:TiO\(_2\) thin films. The resistivity \( \rho_{\text{xx}} \) is of the order of 0.1 Ω cm, while the OHE (Fig. 3, top panel) yields a carrier density of \( 5 \times 10^{18} \) cm\(^{-3} \) and a Hall mobility of

![FIG. 2. Cross-sectional TEM images of a pure anatase Co:TiO\(_2\) film of 75 nm. Top panel: Lattice image with two anatase lattice planes overlaid. Middle and bottom panels: Region of the film near the substrate interface at different resolutions with anatase unit cell overlaid, as well as SAED patterns (bottom left) of the film and the substrate. White arrows in the middle panel indicate low angle grain boundaries.](image1)

![FIG. 3. Total Hall resistivity (top panel) and anomalous Hall resistivity after subtracting the linear OHE term (bottom three panels) for a pure anatase Co:TiO\(_2\) thin film of 185 nm, measured at 280, 160, and 100 K (open symbols). In the second panel the magnetization of the same film measured at \( T = 300 \) K with the field applied perpendicular to the film is also shown (solid symbols).](image2)
17 cm²/V s at room temperature. The mobility is comparable to undoped anatase TiO₂ (Ref. 16) and contrasts with the rather low carrier mobility (~0.1 cm²/V s) associated with rutile TiO₂. The Hall effect of these anatase Co:TiO₂ films having relatively low carrier concentration.

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In conclusion, we have observed the AHE in anatase Co:TiO₂ films that have reasonable mobility and relatively low carrier concentration (~5 × 10¹⁸ cm⁻³). The latter, in combination with the presence of the AHE, gives prospects to examine the role of carriers in the ferromagnetism of anatase Co:TiO₂ under a field effect device configuration. This may clarify the origin of the ferromagnetism in this oxide magnetic semiconductor.

The table below shows the values of σₓₓ, ρ_AHE at saturation, and σ_AHE for 185 nm anatase Co:TiO₂ films at different temperatures.

<table>
<thead>
<tr>
<th>T (K)</th>
<th>σₓₓ(Ω⁻¹ cm⁻¹)</th>
<th>ρ_AHE(μΩ cm)</th>
<th>σ_AHE(μΩ⁻¹ cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>16.3</td>
<td>1.3</td>
<td>345</td>
</tr>
<tr>
<td>160</td>
<td>21.2</td>
<td>1.2</td>
<td>539</td>
</tr>
<tr>
<td>280</td>
<td>15.6</td>
<td>1.2</td>
<td>292</td>
</tr>
</tbody>
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