Anomalous Hall effect in anatase Co:TiO_2 ferromagnetic semiconductor

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The observation of the anomalous Hall effect (AHE) in Co-doped TiO_2 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 ($\sim 17\ cm^2/V\ s$) at room temperature and carrier density of $\sim 5 \times 10^{18}\ cm^{-3}$. 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.[1,2] 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.[3,4] These were monitored using the anomalous Hall effect (AHE),[5,6] 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:TiO_2 DMS,[11–13] but the high carrier density (10^{20}–$10^{22}\ cm^{-3}$) precludes electric field control. On the other hand, the observation of the AHE in the case of Co:TiO_2 in the anatase phase is rare.[14,15]

In this letter we report on the observation of the AHE in anatase $Co_xTi_{1-x}O_2$ ($x=0.014$) at relatively low carrier density. Thin Co:TiO_2 films were grown by pulsed laser deposition on TiO_2 terminated (100) $SrTiO_3$ substrates. Ablation of a $Co_xTi_{1-x}O_2$ ($x=0.014$) target was carried out using a KrF excimer ($\lambda=248$ nm) laser with a fluence of $1.8\ J/cm^2$ at a rate of 5 Hz. The temperature during growth of the films was fixed at 550 °C while the oxygen pressure (P_{ox}) 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 $5\times10\ mm^2$ 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 $\rho_{xy}=R_oB+\mu_0R_sM_\perp$. It comprises the ordinary Hall effect (OHE) term ($R_oB=1/ne$), where R_o 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 ($M_\perp$), the anomalous Hall coefficient (R_s), and the permeability in vacuum (μ_0). Initial measurements were made on a 550 nm Co:TiO_2 thin film at room temperature. The bottom panel of Fig. 1

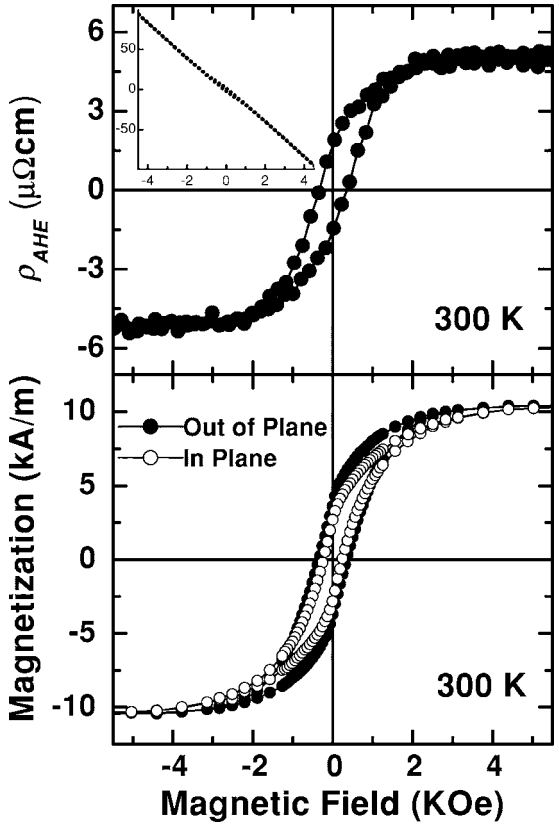

FIG. 1. Top panel: Anomalous Hall resistivity vs the out-of-plane applied magnetic field for a 550 nm Co:TiO_2 thin film. The data are obtained from the total Hall resistivity shown in the inset by subtracting the linear term due to the OHE. The inset has the same units as the main panel. Bottom panel: 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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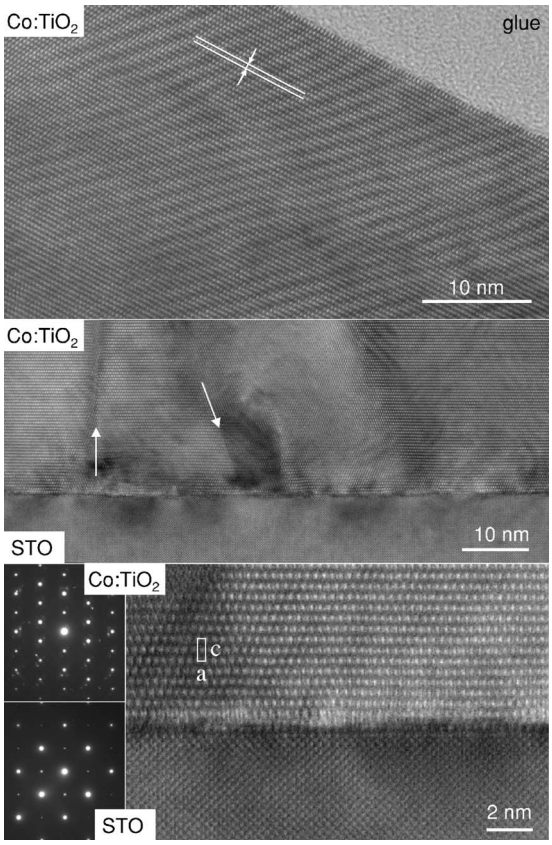

FIG. 2. Cross-sectional TEM images of a pure anatase $Co:TiO_2$ film of 75 nm. Top panel: Lattice image with two anatase lattice planes overlaid. Middle and bottom panels: Region of the film near the substrate interface at different resolutions with anatase unit cell overlaid, as well as SAED patterns (bottom left) of the film and the substrate. White arrows in the middle panel indicate low angle grain boundaries.

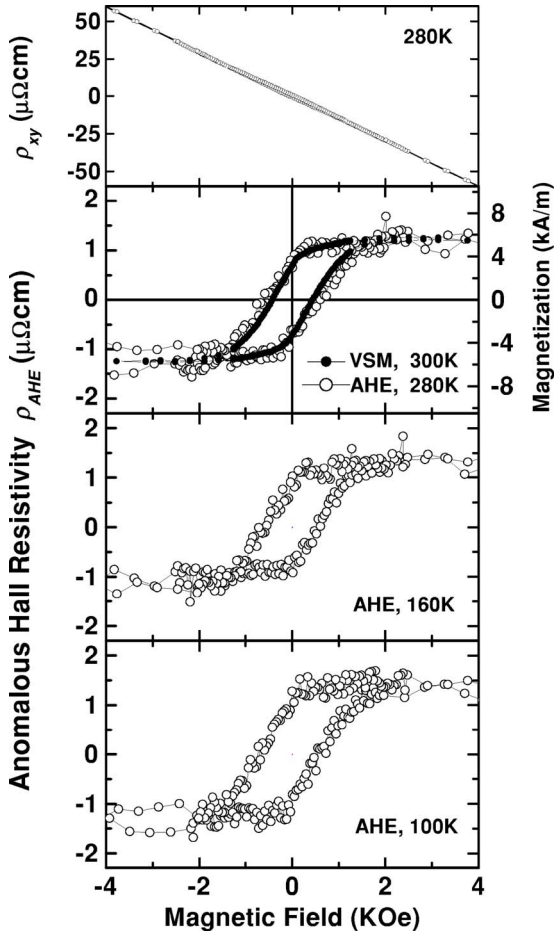

FIG. 3. Total Hall resistivity (top panel) and anomalous Hall resistivity after subtracting the linear OHE term (bottom three panels) for a pure anatase $Co:TiO_2$ thin film of 185 nm, measured at 280, 160, and 100 K (open symbols). In the second panel the magnetization of the same film measured at $T=300$ K with the field applied perpendicular to the film is also shown (solid symbols).

shows the room temperature magnetization measured by VSM with the field applied in plane (open circles) and perpendicular to the film plane (closed circles). 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 ρ_{xy} is linear with a negative slope (see Fig. 1, inset in top panel), 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 (ρ_{AHE}) is plotted against the applied magnetic field. The nonlinearity in the ρ_{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 $M_{\perp}$.

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 $Co:TiO_2$,[13] 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 ρ_{xx} is of the order of 0.1 Ω cm, while the OHE (Fig. 3, top panel) yields a carrier density of 5×10^{18} cm^{-3} and a Hall mobility of

TABLE I. Values of σ_{xx}, ρ_{AHE} at saturation, and σ_{AHE} for 185 nm anatase $Co:TiO_2$ films at different temperatures.

T (K)	$\sigma_{xx}(\Omega^{-1}\,\mathrm{cm}^{-1})$	$\rho_{\mathrm{AHE}}(\mu\Omega\,\mathrm{cm})$	$\sigma_{\mathrm{AHE}}(\mu\Omega^{-1}\,\mathrm{cm}^{-1})$
100	16.3	1.3	345
160	21.2	1.2	539
280	15.6	1.2	292

17 $\mathrm{cm}^2/\mathrm{V\,s}$ at room temperature. The mobility is comparable to undoped anatase TiO_2 (Ref. 16) and contrasts with the rather low carrier mobility ($\sim$0.1 $\mathrm{cm}^2/\mathrm{V\,s}$) associated with rutile TiO_2.[16] The Hall effect of these anatase $Co:TiO_2$ films is nonlinear at low fields. The second panel of Fig. 3 (open symbols) shows ρ_{AHE} at 280 K after subtracting the linear component of the OHE contribution shown in the top panel. The ρ_{AHE} shows hysteresis, switches sign at $\pm$500 Oe, and reaches saturation at $\sim$2.5 kOe. The signal remaining at zero field is about 70% of the value at saturation. The second panel of Fig. 3 also shows the magnetization (solid symbols) in the out-of-plane direction of the same film. The saturation magnetization is found to be 7.5 kA/m, the coercivity is 415 Oe, and the magnetic remanence is $\sim$5 kA/m. A good agreement is found between the behavior of ρ_{AHE} and $M_{\perp}$, establishing a clear room temperature AHE in these anatase $Co:TiO_2$ films having relatively low carrier concentration.

The bottom two panels of Fig. 3 show the AHE measured at 160 and 100 K, respectively. The hysteresis is similar to that at room temperature with slight changes in the saturation value of ρ_{AHE} (see Table I) and the coercivity. Table I also shows the values of the longitudinal conductivity σ_{xx} as well as the anomalous Hall conductivity σ_{AHE}, evaluated[5,13,15] as $\rho_{\mathrm{AHE}}/\rho_{xx}^2$. We can compare these numbers to the data previously reported for rutile $Co:TiO_2$,[13] for which the scaling behavior of the AHE in DMS systems was found to be $\sigma_{\mathrm{AHE}} \propto \sigma_{xx}^{\alpha}$, where the exponent α is related to the scattering mechanism.[5] As already noted previously,[15] our data for σ_{xx} and σ_{AHE} match well with that for rutile $Co:TiO_2$ and lie on the same scaling curve, just as recent AHE data on anatase $Co:TiO_2$ films with an order of magnitude higher conductivity and carrier concentration.[15]

In conclusion, we have observed the AHE in anatase $Co:TiO_2$ films that have reasonable mobility and relatively low carrier concentration ($\sim 5\times 10^{18}$ 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 $Co:TiO_2$ under a field effect device configuration. This may clarify the origin of the ferromagnetism in this oxide magnetic semiconductor.

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