High-temperature ferromagnetism in Co-implanted TiO₂ rutile

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Abstract
We report on structural, magnetic and electronic properties of Co-implanted TiO₂(1 0 0) rutile single crystals for different implantation doses. Strong ferromagnetism at room temperature and above is observed in TiO₂ rutile plates after cobalt ion implantation, with magnetic parameters depending on the cobalt implantation dose. While the structural data indicate the presence of metallic cobalt clusters, the multiplet structure of the Co L₃ edge in the XAS spectra provides evidence that a sizeable portion of the dopants occupy substitutional Co²⁺ sites. The detailed analysis of the structural and magnetic properties indicates that there are two magnetic phases in Co-implanted TiO₂ plates. One is a ferromagnetic phase due to the formation of long range ferromagnetic ordering between implanted magnetic cobalt ions in the rutile phase, and the second one is a superparamagnetic phase which originates from the formation of metallic cobalt clusters in the implanted region. Using x-ray resonant magnetic scattering, the element specific magnetizations of cobalt, oxygen and titanium in Co-implanted TiO₂ single crystals are investigated. Magnetic dichroism was observed at the Co L₂,₃ edges as well as at the O K edge. Anomalous Hall effect measurement indicates n-type carriers in Co-implanted TiO₂ rutile. The interaction mechanism, which leads to ferromagnetic ordering of substituted cobalt ions in the host matrix, is also discussed.

1. Introduction

Oxide-based diluted magnetic semiconductors (DMSs) have recently attracted considerable attention because of reports on the room temperature ferromagnetism (FM) in several systems and their projected potential for spintronic devices [1, 2]. Since Matsumoto et al [3] observed room temperature FM in Co-doped anatase TiO₂, much interest has been focused on titanium dioxide as a host material for magnetic doping. Co-doped TiO₂ has been grown by using a wide variety of growth methods, including pulsed laser deposition (PLD) [4–7], laser molecular beam epitaxy (LMBE) [8–10], combinatorial LMBE [3, 11], reactive co-sputtering [12, 13], magnetron sputtering [14, 15], metal organic chemical-vapour deposition (MOCVD) [16], oxygen plasma assisted molecular beam epitaxy (OPA-MBE) [17–19] as well as the sol–gel method [20]. Both the epitaxial TiO₂ anatase thin film and the single-crystalline TiO₂ rutile have also been doped using the ion implantation technique [21–27]. In addition to different growth techniques, different substrates such as Al₂O₃ [28, 29], SrTiO₃ [4–6, 15,17–19], LaAlO₃ [3, 5, 6, 8, 18], Si [12] and...
SiO₂/Si [16] have been used to synthesize Co-doped TiO₂ films.

Many groups have observed room temperature ferromagnetism in Co-doped TiO₂ for both anatase and rutile phases [2, 3, 6, 12, 13, 22–25, 27, 30, 31]. A Curie temperature of about 650 [6] and 700 K [22] was reported by different groups. Subsequent reports have concentrated on the origin of FM in this material. Spectroscopic studies indicated that cobalt ions in thin TiO₂ films exist in a +2 formal oxidation state, consistent with FM originating from Co substitution on the Ti site [4]. In other publications it is suggested that the ferromagnetic behaviour is due to cobalt clustering depending on the growth conditions [3, 8, 18]. Chambers et al [17] reported that solid solution of Co in TiO₂ is possible at least up to 10% when TiO₂ is deposited on SrTiO₃ substrates. However, when TiO₂ films are grown on LaAlO₃ substrates the solid solution is only about 2–7% [3, 6]. Co metal clusters were observed in the as-grown Co-doped TiO₂ films with a cobalt concentration of about 2%. Post-annealing of the samples leads to dissolving of the clusters in the TiO₂ matrix [6]. For higher cobalt concentrations bigger cobalt clusters were reported with a cluster size of about 150 nm [16].

If the observed FM is indeed due to substituted magnetic elements in the host matrix, then another important question arises, concerning the coupling mechanism which leads to FM. Recently, we have reported the observation of room temperature FM and in-plane magnetic anisotropy of single-crystalline TiO₂ rutile structures after high dose Co implantation [23, 24, 27]. From the observation of the in-plane magnetic anisotropy we concluded that FM in this system results from the incorporation of Co ions in the TiO₂ lattice, but a coexistence with Co nanoclusters could not be excluded.

In order to clarify this situation we studied the structural, magnetic and electronic properties of Co-doped (1 0 0)-oriented rutile TiO₂ single crystals for different implantation doses. The resulting Co:TiO₂ samples have been characterized by Rutherford backscattering spectroscopy (RBS) to obtain the Co depth distribution profiles and by atomic force microscopy (AFM) to check the surface properties after implantation, as well as by x-ray diffraction (XRD) and by high-resolution transmission electron microscopy (TEM) to reveal the presence of precipitates and metallic Co clusters. X-ray absorption spectroscopy (XAS) has also been employed to determine the oxidation state versus the metallic state of the implanted cobalt ions. The magnetic properties of TiO₂ rutile samples have been investigated using the magneto-optical Kerr effect (MOKE), superconducting quantum interference device (SQUID) based magnetometry and x-ray resonant magnetic scattering (XRMS) techniques. In addition, Hall effect measurements were carried out to verify the presence of intrinsic FM and to relate it to the carrier type in the samples.

2. Sample preparation

40 keV Co⁺ ions were implanted into (1 0 0)-oriented 15 × 15 × 1 mm³ single-crystalline TiO₂ rutile substrates (from the Moscow Power Engineering Institute) by using the ILU-3 ion accelerator (the Kazan Physical-Technical Institute of the Russian Academy of Sciences) with an ion current density of 8 µA cm⁻². The implantation dose varied in the range 0.25–1.50 × 10¹⁷ ions cm⁻². The sample holder was cooled by flowing water during the implantation to prevent the samples from overheating. The implanted plates were cut by a diamond cutter into smaller pieces for structural, magnetic and electronic studies. As a last step, four gold contacts were evaporated on the corners of the samples for Hall effect measurements. The Co-implanted TiO₂ samples used in this study are listed in table 1.

3. Experimental results

3.1. Structural properties

In this section, the structural properties of non-implanted and Co-implanted TiO₂ rutile plates are presented. The depth distribution of implanted cobalt ions in the rutile samples as well as the cobalt concentration for each dose are determined using the RBS technique. The RBS measurements were carried out at the Dynamic Tandem Laboratory (DTL) at the Ruhr-Universität Bochum. Figure 1 presents the depth dependence of the cobalt concentration in Co-implanted TiO₂ plates for different Co ion implantation doses. The RBS data show a maximum cobalt concentration of about 25 at% for the highest Co dose and it decreases to about 5 at% for the lowest dose. Due to the ion sputtering of the surface during implantation, the maximum slightly shifts to lower depth for higher dose levels. An extended inward tail up to 70 nm is also observed for each implantation dose due to cobalt diffusion into the volume of the rutile single crystals.

Figure 2 shows small-angle x-ray reflectivity scans taken with synchrotron radiation at the Hamburg Synchrotron Radiation Laboratory (HASYLAB) with an energy of E = 8048 eV. The solid line in figure 2 is a fit to the data points for sample 6 (1.50 × 10¹⁷ ions cm⁻²) from table 2 as obtained by the commercial software WinGIXA, which is based on the Parratt formalism [32]. Since the cobalt concentration in the TiO₂ crystals changes with depth, for fitting of the reflectivity data the implanted area is sliced into five layers. The roughness and electron density values obtained from the fit for each layer are listed in table 2. Aside from the top layer the roughness parameters of the inner layers do not have a real physical relevance aside from smoothing the electron density profile. The model used for fitting perfectly matches the RBS data and figure 3 shows the depth dependence of the cobalt concentration and the normalized electron density (ρe/ρe(TiO₂)) obtained from the fit. The solid line in figure 3...
Figure 1. Cobalt concentration profiles as a function of depth and for different implantation doses measured by RBS.

Figure 2. Small-angle x-ray reflectivity data and fit for sample 6 (1.50 \times 10^{17} \text{ ions cm}^{-2}).

Table 2. Fitting parameters of the reflectivity curve (figure 2) for sample 6 (1.50 \times 10^{17} \text{ ions cm}^{-2}).

| Layer | Thickness (nm) | Roughness (nm) | \(\rho\) (g cm\(^{-3}\)) |
|-------|----------------|---------------|--------------------------|
| 1. layer | 11.2          | 2.68          | 4.229                    |
| 2. layer | 11.1          | 0.050         | 4.234                    |
| 3. layer | 12.1          | 0.071         | 4.227                    |
| 4. layer | 14.2          | 0.01          | 4.200                    |
| 5. layer | 20.3          | 9.05          | 4.180                    |
| Pure TiO\(_2\) | —             | 0.01          | 4.170                    |

The high-angle XRD measurements were also carried out at the HASYLAB in order to detect possible impurity phases in the samples after implantation. The Bragg scans before and after implantation with different doses are shown in figure 4 for (100)-oriented TiO\(_2\) rutile samples. Increase of the implantation dose up to 1.50 \times 10^{17} \text{ ions cm}^{-2} results in two additional peaks which correspond to the (10\,0) and (00\,0\,2) reflections of hcp Co. Below the implantation dose of 1.25 \times 10^{17} \text{ ions cm}^{-2} cobalt nanoclusters cannot be detected by x-ray diffraction. For every implanted sample a tail, indicated by an arrow in figure 4, is present around the main peak of the TiO\(_2\) (200) reflection. This tail results from the expansion of the TiO\(_2\) lattice upon cobalt implantation and is not observed before the implantation. In addition, a new peak is present on the low angle side, corresponding to the spinel cobalt oxide (Co\(_3\)O\(_4\)) phase reported already by Khaibullin et al in Co-implanted TiO\(_2\) [31]. Due to the difference in etching rates of Co and the TiO\(_2\) during high dose ion implantation [31], cobalt nanoparticles form on the surface and become oxidized forming antiferromagnetic Co\(_3\)O\(_4\) with a Néel temperature of about 40 K. Figure 5 presents the surface morphology of sample 5 (1.25 \times 10^{17} \text{ ions cm}^{-2}) probed by AFM (Digital Instruments NanoScope MultiMode AFM). The AFM image clearly shows a network of cobalt oxide islands on the surface.
there is another cobalt rich layer of about 40 nm thickness. Element specific TEM measurements indicate that the cobalt concentration in this layer is much lower than in the surface layer in agreement with the RBS and x-ray reflectivity data (figure 3).

3.2. Magnetic properties

3.2.1. In-plane magnetic anisotropies and hysteresis measurements. In order to investigate the in-plane magnetic anisotropy of the implanted samples we used a high-resolution MOKE setup in the longitudinal configuration with s-polarized light [34–36]. The MOKE setup allows for a rotation of the sample around its surface normal (by the angle $\varphi$) and perpendicular to the in-plane magnetic field, thus providing information about the in-plane magnetic anisotropy. In figure 7 is shown the in-plane magnetic anisotropy of the samples doped with different doses. Plotted in a polar diagram are the remanent Kerr signal normalized to the Kerr signal at saturation ($\theta_{K}^{\text{rem}}/\theta_{K}^{\text{sat}}$) and the coercive field ($H_{C}$), both at room temperature. For the sample with the highest dose, both, the remanent Kerr signal and the coercive field are reduced to almost zero near the hard axis ($\varphi = 0^\circ$–$180^\circ$), while for the magnetic field applied along the easy axis ($\varphi = 90^\circ$–$270^\circ$) they are close to unity. It is evident from figure 7 that both $\theta_{K}^{\text{rem}}/\theta_{K}^{\text{sat}}$ and $H_{C}$ exhibit a strong two-fold anisotropy for the highest dose which decreases with decreasing implantation dose.

Hysteresis loops of the Co-implanted TiO$_2$ samples, obtained by using a Quantum Design MPMS XL SQUID magnetometer, are presented in figure 8 for 300 K and in figure 9 for 5 K. For both measurements the field is applied parallel to the easy axis. At the highest dose ($1.50 \times 10^{17}$ ions cm$^{-2}$) a square-like hysteresis curve is observed with a large coercive field of $H_{C} = 950$ Oe. A rather sharp magnetization reversal takes place for this sample with a small step at 260 Oe. For the samples implanted with intermediate ion doses ($1.00–1.25 \times 10^{17}$ ions cm$^{-2}$), the recorded $M$–$H$ loops also show hysteretic behaviour, but the coercive fields are decreased significantly. The remanent magnetization normalized to the saturation magnetization is also decreased for the intermediate doses. At 5 K the two step feature in the hysteresis curve is not only present for the highest dose but also for intermediate doses (figure 9). The low dose implanted samples exhibit at low temperatures a typical superparamagnetic behaviour with a pronounced paramagnetic contribution to the hysteresis curves.

The steps in the hysteresis loops are a clear sign for a two-component system. We have therefore simulated the field dependence of the magnetization curves using the formula proposed by Geiler et al [37]:

$$
\frac{M}{M_s} = f_1 \frac{2}{\pi} \arctan \left( \frac{M \pm H_{C1}}{H_{T1}} \right) + f_2 \frac{2}{\pi} \arctan \left( \frac{M \pm H_{C2}}{H_{T2}} \right).
$$

Here $M_s$ is the saturation magnetization of the samples under study, $f_1$ and $f_2$ are weight factors of the first and second magnetic phase that are characterized by the coercive fields ($H_{C1}$, $H_{C2}$) and the threshold values of the magnetic anisotropy.
Figure 7. Left: azimuthal dependence of the remanent Kerr angle normalized to the Kerr angle in saturation; right: azimuthal dependence of the coercive field. All measurements were taken at room temperature for different Co ion doses. Note that in the right panel the centre corresponds to $-0.25\,\text{kOe}$, such that the zero coercivity observed for sample 3 lies on a circle around the negative centre.

Figure 8. SQUID hysteresis loops for different Co ion doses taken parallel to the easy axis at $T = 300\,\text{K}$. The hysteresis loops are normalized to the saturation magnetization. The solid lines are a fits to the hysteresis loops with a two-component line shape according to equation (1).

field ($H_{1c}$, $H_{2c}$), respectively \cite{37}. This expression describes the behaviour of the magnetic phases very well as seen by the solid lines through the measurement points. The parameters of the simulation for all ferromagnetic samples are listed in table 3. Similar results are obtained for the hysteresis curves measured at 5 K. However, at 5 K the second component starts to contribute already at a dose level of $0.75 \times 10^{17}\,\text{ions cm}^{-2}$. We attribute the first component to the paramagnetic or superparamagnetic cluster contribution and the second component with a much higher coercive field and sharp magnetization reversal to the intrinsic ferromagnetic part.

From table 3 it may also be noticed that the coercivity of the cluster fraction first decreases with increasing dose and then increases again with a minimum at $0.75 \times 10^{17}\,\text{ions cm}^{-2}$. This behaviour may be understood by a change of the cluster shape. For essentially zero coercivity the clusters are expected to have spherical shape and a blocking temperature at or above room temperature. While the blocking temperature for sample 3 is indeed at room temperature (see figure 10), the spherical shape needs further experimental confirmation via TEM studies.

In order to further investigate both magnetic components, their coexistence and prevalence with implantation dose, we have performed temperature dependent magnetization ($M–T$) measurements using a SQUID magnetometer. Figure 10 presents field cooled (FC) and zero field cooled (ZFC) plots for each sample. For ZFC measurements, the samples are cooled in zero field to 5 K and the magnetization is recorded during
Figure 9. SQUID hysteresis loops for Co-implanted TiO$_2$ samples measured at 5 K along the easy axis. The hysteresis loops are normalized to the saturation magnetization. The solid lines are fits to the hysteresis loop with a two-component line shape according to equation (1).

Table 3. Fitting parameters of magnetic hysteresis curves taken at 300 K for samples 1–6.

| Dose ($\times 10^{17}$ ions cm$^{-2}$) | $f_1$ (%) | $H_{C1}$ (±5 Oe) | $H_{T1}$ (±10 Oe) | $f_2$ (%) | $H_{C2}$ (±5 Oe) | $H_{T2}$ (±10 Oe) |
|--------------------------------------|----------|-----------------|-----------------|----------|-----------------|-----------------|
| 0.25                                 | 100      | 63              | 543             | 0        | 0               | 0               |
| 0.50                                 | 100      | 32              | 578             | 0        | 0               | 0               |
| 0.75                                 | 100      | 4               | 350             | 0        | 0               | 0               |
| 1.00                                 | 98       | 92              | 250             | 2        | 350             | 19              |
| 1.25                                 | 90       | 329             | 249             | 10       | 500             | 184             |
| 1.50                                 | 46       | 257             | 348             | 54       | 983             | 17              |

warming up to 390 K in an applied field of 100 Oe parallel to the film surface. For FC measurements the applied field of 100 Oe is kept constant during cooling to 5 K and the magnetization is recorded during field warming within the same field value. The FC (black squares) and ZFC (grey circles) curves diverge substantially for all doses and the peak in the ZFC curve progressively shifts to higher temperatures with increasing cobalt concentration. This behaviour is not expected for a ferromagnet and suggests the presence of magnetic cobalt nanoparticles in the films or a spin-glass like nature of the system [38, 39]. The $M$–$T$ curve of sample 1 ($0.25 \times 10^{17}$ ions cm$^{-2}$) is rather unusual and may be attributed to the coexistence of a weak ferromagnetic and a superparamagnetic phase with a transition temperature of about 30 K. The $M$–$T$ curves for films with higher cobalt concentrations ($0.50–0.75 \times 10^{17}$ ions cm$^{-2}$) indicate the occurrence of superparamagnetism with a blocking temperature of about 100 K and 250 K for sample 2 ($0.50 \times 10^{17}$ ions cm$^{-2}$) and sample 3 ($0.75 \times 10^{17}$ ions cm$^{-2}$), respectively. The temperature dependence of sample 4 magnetization is similar to that of sample 2 and sample 3 except that the blocking temperature is much higher, namely above 390 K. It is also important to note that the FC curve of sample 4 shows a more or less monotonic behaviour versus temperature which is typical for ferromagnets. The reported room temperature FM with a two-fold in-plane magnetic anisotropy indicates that for this dose (sample 4: $1.0 \times 10^{17}$ ions cm$^{-2}$) substituted cobalt ions start to interact ferromagnetically. The FC and ZFC curves of sample 5 ($1.25 \times 10^{17}$ ions cm$^{-2}$) and sample 6 ($1.50 \times 10^{17}$ ions cm$^{-2}$) are much closer to each other. This progression indicates that the ferromagnetic phase becomes dominant in these samples. The observation of a two-component hysteresis at RT for sample 6 supports this argument. Small peaks in the ZFC curves at low temperatures of sample 6 indicate the existence of superparamagnetic cobalt clusters. These clusters are also clearly seen in the TEM images of sample 6 (figure 6).

3.2.2. XRMS and XAS measurements. To shed more light on the origin of room temperature FM in Co-implanted TiO$_2$ rutile films, the magnetic properties have also been investigated using the XRMS and XAS techniques. Both the XRMS and XAS experiments were carried out at the undulator beam lines UE56/1-PGM and UE52-SGM at BESSY II (Berlin, Germany) using the ALICE diffractometer [40]. The diffractometer comprises a two circle goniometer and works in horizontal scattering geometry. A maximum magnetic field of ±2700 Oe can be applied in the scattering plane along the sample surface.
Figure 10. FC (black squares) and ZFC (grey circles) magnetization curves of Co-implanted TiO$_2$ rutile samples recorded with a SQUID magnetometry. 

either parallel or antiparallel to the photon helicity, which corresponds to the longitudinal magneto-optical Kerr effect (L-MOKE) geometry. The magnetic contribution to the scattered intensity (XRMS) was always measured by reversing the magnetic field direction while keeping the photon helicity fixed. Thus, by tuning the energy to the Co $L_3$ absorption edge (780 eV), reflectivity scans were taken and the magnetic splitting for plus and minus field was clearly seen (presented in [25]). As a compromise between high scattering intensity and high magnetic sensitivity for the investigation of the magnetic properties via energy scans at the Co $L$ edges, the scattering angle was fixed at the position of $2\theta = 8.2^\circ$ (the angle of incidence $\theta = 4.1^\circ$) [25]. For measurements at the O K edge ($E = 535$ eV) the scattering angle was fixed at $2\theta = 12^\circ$, which corresponds to the same scattering vector in the reciprocal space.

First, we measured the energy dependence of the scattered intensity (XRMS) in an energy range covering the Co $L_{2,3}$ edges. Since the magnetic contribution to the resonant scattering can best be visualized by plotting the asymmetry ratio ($A_r = (I^+ - I^-)/(I^+ + I^-)$), in figure 11 we present the dose dependence of the asymmetry ratio at the Co $L$ edges measured in saturation at room temperature. Only the lowest dose of $0.25 \times 10^{17}$ ions cm$^{-2}$ is measured at 30 K. The magnetization of the samples decreases by decreasing the Co ion dose in agreement with SQUID hysteresis curves and previous MOKE measurements [27]. It is important to note that the fine structure around the Co $L_3$ edge, which is clearly seen in the asymmetry ratio in figure 11 for sample 6, is not typical for metallic cobalt. It is well known that in the case of metallic films the absorption spectra around the $L_3$ peak of Co consist of a single component [41]. This fine structure of the Co $L_3$ peak is similar to that observed before for CoO films [41], and it is indicative of a Co$^{2+}$ state. To make this situation more clear and to record comparable results with previous reports [8], we performed XAS experiments. The absorption data were taken by the total electron yield (TEY) method, i.e. by measuring the sample drain current. Since the external magnetic field changes the excited electron trajectories, the XAS spectra were measured by reversing...
photon helicity in remanence. The angle of incidence was set again to $4.1^\circ$ with respect to the surface. The absorption spectra were normalized to the incoming photon flux measured from the beam line mirror. The averaged x-ray absorption spectra $(\sigma^+ + \sigma^-)/2$ at the Co $L_{2,3}$ edges is shown in figure 12. The XAS spectrum clearly shows a multiplet structure at the Co $L_3$ edge. This multiplet structure is a strong indication of a sizeable portion of Co ions being in the Co$^{2+}$ state in this sample. The other contribution is from Co metal clusters with a fractional contribution of about 50% according to the decomposition of the corresponding magnetic hysteresis reported in table 3.

The magnetic signal at the Ti $L_{2,3}$ and the O $K$ edges was also investigated for sample 6. Figures 13 and 14 show the corresponding asymmetry ratios. Within the sensitivity limit no magnetic signal could be recorded neither for Ti nor for O at room temperature. However, at the O $K$ edge, a small but clearly visible magnetic signal was observed at $T = 30$ K [25]. It should be mentioned that the oxygen polarization has also been observed at low temperatures for samples with lower dose (dose levels of $1.00 \times 10^{17}$ ions cm$^{-2}$). For samples implanted with doses below $1.00 \times 10^{17}$ ions cm$^{-2}$, the magnetic signal at the O $K$ edge is below the sensitivity limit of the experimental setup.

3.2.3. High-temperature magnetization experiments. In order to determine the Curie temperatures ($T_C$) of Co:TiO$_2$ samples, we have carried out thermo-magnetic measurements using the Faraday balance technique [42] by heating the samples from 100 K (ZFC) up to 1000 K with a rate of 100 K min$^{-1}$ in air and at an applied field of 2 kOe. In figure 15 we show the magnetization curves for TiO$_2$ rutile plates implanted with different doses. The sample with a dose of $0.50 \times 10^{17}$ ions cm$^{-2}$ shows the magnetic/non-magnetic transition temperature at about 850 K (curve 1). For samples 4 ($1.00 \times 10^{17}$ ions cm$^{-2}$) and 6 ($1.50 \times 10^{17}$ ions cm$^{-2}$), two magnetic ordering temperatures of $T_{C1} \sim 700$ K and $T_{C2} \sim 850$ K were observed (curves 2 and 3). This shows that two ferromagnetic phases, a ‘low temperature’ and a ‘high-temperature’ phase, coexist in these samples. The contribution to the magnetization from the high-temperature phase decreases gradually with increasing cobalt implantation dose. Finally, for the sample with the highest dose of $1.50 \times 10^{17}$ ions cm$^{-2}$, the low-temperature phase dominates, while the high-temperature phase gives only a minor contribution (curve 3).

It should be stated here that the high-temperature magnetization curves presented in figure 15 are irreversible, i.e. on cooling down the ferromagnetic signal disappears. From this we infer that some diffusion process and oxidation of Co nanoparticles may occur. Thus the high-temperature transition temperatures should not be confused with a real Curie temperature. Furthermore, the magnetization versus temperature does not follow the shape of a usual order parameter. On the other hand, after vacuum annealing the samples at high temperatures [31], $T_{C1}$ reappears but not $T_{C2}$, indicating that $T_{C1}$ is more intrinsic than $T_{C2}$. Thus the $T_{C1}$ phase recovers after high-temperature annealing, albeit with a reduced remanent magnetization of 10–20% at room temperature. This point clearly needs some further investigations. For the present purpose, it is important to note that a stable ferromagnetic phase exists at room temperature and far above, which may be very useful for high-temperature applications of DMSs.
4. Hall effect measurements

The observation of an anomalous Hall effect (AHE) is suggested to be one of the important criteria for DMS materials being intrinsically ferromagnetic [43, 44]. In the past, several groups reported the AHE in highly reduced TiO2 films doped with either with Co or Fe, from which they infer the possibility of intrinsic FM in these samples [7, 9, 45]. However, recently, Shinde et al [46] reported the co-occurrence of superparamagnetism and AHE in highly reduced Co-doped TiO2 rutile films, raising questions about the usefulness of the AHE as a test of the intrinsic nature of FM in DMS materials without a detailed characterization of the sample.

In magnetic materials, in addition to the ordinary Hall effect (OHE), there is an additional voltage proportional to the sample magnetization [47], the so-called AHE. Hence, the Hall voltage can be written as follows [47]:

\[ V_{\text{H}} = \left( \frac{R_0 I}{t} \right) H \cos(\alpha) + \left( \frac{R_A I}{t} \right) M \cos(\theta), \]

where \( t \) is the film thickness and \( I \) is the current. \( R_0 \) and \( R_A \) are the ordinary and anomalous Hall effect coefficients, respectively. \( \mu_0 \) is the permeability of free space. \( \alpha \) is the angle between the applied magnetic field \( (H) \) and the film normal. \( \theta \) is the angle between the sample magnetization \( (M) \) and the sample normal. The first term in equation (2) is the OHE and arises from the Lorentz force acting on conduction electrons. This establishes an electric field perpendicular to the applied magnetic field and to the current. The second term is the AHE and it is conventionally attributed to spin dependent scattering mechanism involving a spin–orbit interaction between the conduction electrons and the magnetic moments of the material. At low applied magnetic fields, the Hall voltage \( (V_{\text{H}}) \) is dominated by the magnetic field dependence of the sample magnetization \( M \). When the applied magnetic field is high enough to saturate the sample magnetization, the magnetic field dependence of the Hall voltage becomes linear due to the OHE.

The Hall effect measurements were carried out at 4.2 K using a van der Pauw configuration presented in figure 16 as an inset. In spite of the fact that the structural and the magnetization measurements indicate the presence of magnetic nanoparticles in the Co-implanted TiO2 films, the AHE is observed for these samples. The Hall effect data of sample 6 are shown in figure 16. As it is explained above, a rapid increase in the Hall voltage at low fields can be interpreted as an AHE which is followed by a slow decrease corresponding to the OHE. It is important to note that the negative slope of the high field data indicates n-type carriers in Co-implanted TiO2 rutile. The electron density \( (n) \), calculated from the slope of the curve at higher fields, is about \( 3.75 \times 10^{18} \text{ cm}^{-3} \).

5. Discussion

The origin of the observed two ferromagnetic phases in Co-implanted TiO2 rutile plates is attributed to the formation of two cobalt enriched layers with different concentrations and valence states of the cobalt dopant. The TEM images (figure 6) clearly show that nanosize magnetic particles of cobalt metal nucleate in the surface region of the implanted rutile where the cobalt concentration is maximal (see RBS data in figure 1). Mostly beneath this layer, in the tail of the depth distribution profile, the implanted cobalt can exist in an ionic state substituting the Ti3+ ions in the matrix by Co2+ ions. For charge neutrality the oxygen vacancies should provide compensation of local charge because of the valence mismatch. At the lowest dose \((0.25 \times 10^{17} \text{ ions cm}^{-2})\) the magnetic contribution from the metallic cobalt clusters and the substituted cobalt ions is very small, and hence the MOKE signal at room temperature is rather weak. Increasing the cobalt implantation dose leads to both, an increase of the Co cluster size, as seen by the increasing blocking temperature, and to more substitutional cobalt in the Co2+ state. At certain concentrations the substituted cobalt ions start to interact leading to FM at room temperature in sample 4 \((1.00 \times 10^{17} \text{ ions cm}^{-2})\) and sample 5 \((1.25 \times 10^{17} \text{ ions cm}^{-2})\). At doses higher than \(1.25 \times 10^{17} \text{ ions cm}^{-2} \) strong ferromagnetic order is formed due to the ion accumulation and indirect exchange interaction between the Co2+ ions. However, TEM images, peaks in the ZFC curves, and two-component hysteresis curves for dose levels 1.25–1.50 \( \times 10^{17} \text{ ions cm}^{-2} \) indicate that cobalt nanoparticles coexist with the bulk ferromagnetic phase. According to table 3 for sample 6 the proportion between cluster magnetism and intrinsic FM is about 50% : 50%.

Revealing the interaction mechanism of substituted cobalt ions which leads to FM in Co:TiO2 is also an important incentive of this study. Since the XAS spectra clearly show the multiplet structure of the Co L3 peak (see figure 12), it is certain that some portion of the implanted cobalt ions in TiO2 rutile are in the Co2+ oxidation state. When TiO2 is doped with cobalt ions, simultaneously oxygen vacancies are also expected to be produced [48]. The observation of the AHE in the Co-implanted rutile samples gives clear evidence for oxygen vacancies which contribute to shallow donor states in TiO2 and increase the carrier density [49]. It was suggested that these oxygen vacancies strongly promote FM in Co-implanted TiO2.

![Figure 16. Hall effect data of sample 6 taken at 4.2 K. Inset shows the geometry of the Hall effect experiments.](image-url)
films by an indirect exchange of substituted cobalt ions through
electrons trapped by neighbouring oxygen vacancies [50].
We have also noticed a clear polarization of the oxygen
p-orbitals in Co-implanted TiO$_2$ rutile samples. The shape of
the hysteresis curve and the coercive field measured at the O
K edge is the same as the one recorded at the Co L$_2$ edge [25].
This is a clear indication that oxygen ions, which are close to
Co ions in TiO$_2$ become magnetically polarized. Whether the
oxygen polarization is essential for supporting ferromagnetic
exchange is presently not clear.
Another important result of this study is the observation of an
AHE. The AHE is often taken as evidence that the charge carriers are polarized and that the material is a true DMS. However, after simultaneous observation of superparamagnetism and AHE in Co-doped TiO$_2$ films by Shinde et al [46] and also in this study, the existence of an
AHE can be thought of as a necessary measurement condition but it is not sufficient by itself to claim the intrinsic nature of
FM in a DMS material.

6. Summary and conclusions
In conclusion, we have studied in detail the structural,
and magnetic properties of Co-implanted TiO$_2$ rutile
films for different implantation doses. The structural data clearly show that cobalt clusters are present in the samples
after high dose cobalt ion implantation. In addition to the
cluster formation, substitution of cobalt ions into the
rutile lattice is also confirmed by XAS experiments. The
origin of the observed magnetic behaviour in the samples
is explained by the coexistence of two different magnetic
phases. Cobalt nanoparticles in the surface layer form a
superparamagnetic phase in the samples implanted with low
and intermediate doses. In addition, substitution of Ti$^{4+}$
ions by Co$^{2+}$ ions leads to intrinsic FM as a second magnetic
phase. The oxygen vacancies formed by ion implantation provide charge compensation and serve as mediators for the exchange interaction between the Co$^{2+}$ ions in high dose doped
samples. The observation of the AHE in Co-implanted TiO$_2$
rutile can also be thought of as an important indicator of the
observed long range ordered intrinsic FM in the rutile
phase. At the highest dose, a strong ferromagnetic phase exists
with a Curie temperature of above 700 K. This ferromagnetic
phase exhibits a perfect uniaxial in-plane magnetic anisotropy
following exactly the crystal symmetry of the TiO$_2$ rutile. We
consider this as the strongest experimental evidence for the
intrinsic nature of FM in the Co-doped TiO$_2$ rutile.

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