Iron and cobalt co-doping of single crystalline titanium dioxide

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Abstract. Single-crystals of TiO₂ rutile were co-implanted with iron and cobalt to investigate the interplay between the role of these ions and their influence in the magnetic properties of the system. In the co-implanted crystals, both ions were implanted with the same nominal fluence, \(5 \times 10^{16}\) cm\(^{-2}\), and an implantation energy of 150 keV. The as-implanted single crystals exhibited superparamagnetic behaviour associated with the formation of nanosized aggregates. An annealing treatment at 1073 K induced recovery of the lattice structure and the appearance of a ferromagnetic phase. The evolution of the systems depends on the order of implantation of the two different ions.

1. Introduction

Wide band gap semiconductors doped with magnetic ions offer one of the possible routes to obtain diluted magnetic semiconductors (DMS). One of the candidate systems, and also one of the most studied oxides, is TiO₂, both in rutile and anatase phases. The role of iron and cobalt single implantations in rutile is known to be significantly different. Doping rutile with Co, results in the formation of magnetic nanosized aggregates, with sizes that increase after annealing in vacuum. Reported results for Co implanted rutile indicate that the presence of oxygen vacancies is important to stabilize the nanosized metallic aggregates in the structure. For Fe doping, although aggregates can be found after implantation, thermal treatments in vacuum induce the formation of a ternary compound Ti-Fe-O, consistent with the high affinity for Fe binding with oxygen. As to the joint role of these two magnetic ions, it is known that iron-cobalt alloys have high values of saturation magnetisation, and the coexistence of both ions improves the ferromagnetic interactions. Average magnetic moments per magnetic ion are between 2-2.4\(\mu_B\) for a large range of compositions.

In this work, results for rutile co-doped with Co and Fe are presented. The purpose of the co-implantation is to stabilize the position of cobalt ions by the influence of iron that should inhibit cobalt...
aggregation by decreasing the concentration of oxygen vacancies as a consequence of the high affinity for Fe binding with oxygen.

2. Experimental details

Single crystals of rutile were implanted at room temperature (= 295 K) with 150 keV ions of Co and Fe, to a total nominal fluence of $1 \times 10^{17}$ cm$^{-2}$ ($5 \times 10^{16}$ cm$^{-2}$ Co + $5 \times 10^{16}$ cm$^{-2}$ Fe). Two types of samples were produced: one by implanting first Co and afterwards Fe, designated “Co+Fe” in the text, and the other by implanting the ions in reverse order, named “Fe+Co”.

Rutherford Backscattering Spectrometry (RBS), combined with the channelling effect (RBS-C), and X-Ray Diffraction (XRD) were used as structural and compositional characterization techniques, while Particle Induced X-ray Emission (PIXE) analysis was used to assist quantifying the amount of implanted ions. To characterize the magnetic behaviour of the samples, magnetic moment measurements were carried out using a Quantum Design MPMS magnetometer, for applied magnetic fields up to 5.5 T and temperatures between 2 K and 400 K. Measurements as a function of temperature were carried out for increasing temperature after cooling in zero field (ZFC) and in the measurement field (FC).

The characterization of one un-implanted single crystal of the same batch as the implanted ones, allowed the confirmation of the expected Van Vleck paramagnetic behaviour of rutile, giving an average magnetic susceptibility of $8.0 \times 10^{-10}$ m$^3$/kg. For the implanted samples, the magnetic moment results are considered the sum of two independent contributions: a paramagnetic component assigned to the un-implanted volume of TiO$_2$ and the contribution of the implanted region. The paramagnetic moment of the un-implanted volume was calculated using the measured susceptibility and the mass of the crystal, since the mass of the implanted region is below 0.01% the total mass. This contribution was subtracted in all the experimental results presented, in order to isolate the behaviour of the implanted region. The measurements were carried out along [010] TiO$_2$ crystalline direction, in all samples.

An annealing treatment at 1073 K for one hour in vacuum was carried out for all the samples in order to allow the recovery of the crystalline structure and rearrangement of the implanted ions.

3. Experimental results and discussion

Figure 1 presents the RBS results for a Co+Fe sample obtained with an incident beam aligned with the [100] TiO$_2$ axis and with an incident beam in a random direction (i.e. a non-channelling direction, one which is close to but non-aligned with the [100] direction). The high yield in the aligned spectrum, observed for the implanted region (I) as compared with the one for the un-implanted region (II) shows a strong dechannelling by the host lattice indicating that it became highly damaged due to the implantation procedure. The RBS results for Fe+Co implantation are similar.

The presence of Fe and Co is clear from the edge position at channel 525 and its shape near channel 510. Further analysis of the RBS spectra showed that the highly damaged surface region where the implanted ions stopped extends in both cases to 140 nm depth.

PIXE analysis was used to help quantifying the number of implanted ions measuring a fluence of $5 \times 10^{16}$ cm$^{-2}$ for Fe and a lower fluence, around $3 \times 10^{16}$ cm$^{-2}$, for Co, in all
samples, independently of the sequence of implantation. The amount of implanted cobalt is therefore approximately half that of the implanted iron, although equal nominal values were used for both atomic species. The PIXE analysis was also carried in the intermediate state, after implantation of the first ion species and before the implantation of the second one. Again, the measured retained fluences were similar, indicating that the lower fluence of cobalt is not a consequence of the presence of iron, since it is also measured in a Co-only implanted sample.

Magnetization as a function of temperature and magnetic field is presented in figures 2 and 3 for one Fe+Co sample, the sample Co+Fe displaying similar dependences. The presence of a blocking temperature in the M(T) curves, along with too high values calculated for the magnetic moment when a Curie dependence is fitted to the paramagnetic regime, indicate that the implanted region is superparamagnetic and, consequently, the as implanted state of both samples is dominated by the presence of nanosized magnetic aggregates. Using the saturation value of the magnetization curves, and assuming that the aggregates are essentially of metallic iron and cobalt, with magnetic moments around $2.0(2) \mu_B$, we can calculate that a fraction of the order of 50% of the implanted ions is incorporated into these aggregates. The measured blocking temperatures are 24 K in the case of Fe+Co, and 40 K for the Co+Fe samples, indicating that the magnetic aggregates have smaller sizes in the former samples. To access the structure of the implanted region, XRD spectra were obtained. The results display the (200) peak of the rutile structure (as expected for (100) single crystals). The TiO$_2$ peak is the only one detected after implantation of the first ion, indicating that other phases are not formed or aggregates are too small. After the implantation of the second ion two broad peaks appear at angles $2\theta$ around 35° and 76°. There are several phases compatible with these diffraction peaks, the most likely being spinel structured oxides with iron and cobalt.

The samples were then subjected to a thermal treatment at 1073 K in vacuum, for one hour. The RBS spectra obtained after this annealing (fig. 4) indicate partial recovery of the lattice along with diffusion of the implanted ions. In fact, loss of part of the edge structure recorded close to channel 525 in the RBS spectra of the as-implanted samples, and its apparent displacement to lower energy channels, retaining an edge close to channel 510, suggests that Co ions have moved from the near surface region while Fe ions stay in place. Analysis of these spectra indicate that cobalt diffuses differently, overlapping the Fe depth profile more extensively in the case of Fe+Co samples. PIXE results show that most of the implanted ions stay in the host, confirming inwards diffusion.
Magnetization as a function of temperature is presented in Fig. 5 for the two types of samples. In both cases there is coexistence of antiferromagnetic and ferromagnetic components, confirmed by the behaviour of the magnetization curves at high fields (not shown). The most significant difference is the higher magnetic moment detected for the Fe+Co sample displaying a strong irreversibility up to 350 K. The magnetization as a function of magnetic field shows a ferromagnetic contribution one order of magnitude higher in the case of this sample. A spinel structured ferrite of the type Fe$_2$CoO$_4$ is probably responsible for the ferromagnetic contribution observed for temperatures up to 380 K, but the present results cannot exclude other compounds with similar structure. Clearly, if present in the Co+Fe sample, this phase has a weaker expression.

In summary, this work allows concluding that the effect of implanting the two types of ions is clearly different when compared with Fe and Co implantations separately, but also that the order of implantation is determinant for the final magnetic properties of the system. Further work in order to understand the role of the two ions and identify the spinel phase is in progress.

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