Magnetism in wide band gap semiconductors implanted with non-magnetic ions

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Abstract. Single crystals of ZnO, TiO₂ and LaAlO₃ have been implanted with Ar with 100 keV and different fluencies. The Ar implanted crystals showed a week ferromagnetic-like signal between 10 K and 400 K. Hysteresis curves obtained at room temperature allowed confirming the ferromagnetic behaviour of the implanted samples. Spin polarised first principles density functional calculations were performed in the case of ZnO considering Zn interstitials and O vacancies. No net magnetic polarisation was found for O vacancies, but in the case of Zn vacancies a magnetic moment of 1µ₅B was obtained.

1. Introduction
Diluted magnetic semiconductors (DMS), in which ferromagnetism arises from the doping of a non-magnetic semiconductor with a transition metal element, was first predicted by T. Dietl in oxide systems for the case of Mn-doped ZnO [1]. The large amount of experimental and theoretical work that followed Dietl’s calculation has been far from conclusive with a wide spread of results published by different groups. One of the most discussed issues in these systems is the formation of secondary phases that could be responsible for many of the reports of ferromagnetism in magnetic semiconductors [2,3]. However, the presence of ferromagnetic ordering in a variety of systems that do not include magnetic elements [4,5], together with band structure calculations showing that cation vacancies may be associated with a magnetic moment [6,7], has highlighted the possible contribution of structural defects to the observed magnetic signal. In ZnO, ferromagnetism has been observed in doped systems with structural defects such as thin films [8] and implanted crystals [9], and in non-doped ZnO nanoparticles capped with different organic molecules [10].

In this work the implantation of Ar into ZnO, TiO₂ and LaAlO₃ single crystals was carried out in order to investigate the role of the induced defects in the magnetic properties of the material.

2. Experimental
Single crystals of ZnO, TiO₂ and LaAlO₃ were implanted at room temperature with Ar ions of energy 100 keV using different fluencies as shown in Table 1

| Single Crystals | ZnO Fluence | TiO₂ Fluence | LaAlO₃ Fluence |
|-----------------|-------------|--------------|---------------|
| ZnO             | 1x10¹⁶      | 1x10¹⁷       | 1x10¹⁷        |
| TiO₂            | 1x10¹⁷      | 2x10¹⁷       |               |
| LaAlO₃          | 1x10¹⁷      | 2x10¹⁷       |               |
The implantation procedure with these high fluencies induces disorder in the implanted region. To recover the crystalline structure thermal annealing treatments were carried out at temperatures related with the recovery stages of each lattice. The magnetic behaviour of the virgin crystals and implanted samples was analyzed through magnetization measurements performed with a Squid magnetometer. Rutherford Backscattering Spectroscopy (RBS) and RBS-C were used to investigate the implantation profiles and the lattice induced disorder. Particle induced X-ray emission (PIXE) was also used to check for the presence of impurities.

3. Results and Discussion

For all samples a ferromagnetic component was detected after implantation. In Figure 1 the results obtained for the magnetisation as a function of applied field measured at room temperature for the virgin crystals are presented. The magnetic susceptibilities (M/H) of the virgin crystals, determined at different temperatures, are found to agree within 3% with reported values [11, 12].

Figure 1. Room temperature magnetisation of oxide non implanted single crystals.

Figure 2. Hysterisis curves for the three oxides after implantation with argon with a fluence of 1x10^{17} cm^{-2}. 
In Figure 2 hysteresis curves are presented for the $1 \times 10^{17}$ cm$^{-2}$ implanted samples at 300 K. The results evidence the presence of ferromagnetic behaviour at low fields and, as major contribution, the diamagnetic (paramagnetic in the case of TiO$_2$) signal attributed to the non-implanted volume. For the samples implanted with different fluencies the results are similar. In order to isolate the magnetic contribution of the implanted region, the diamagnetic (paramagnetic) signal of the non-implanted part was subtracted from the raw measurements. Since the implanted region is only a very small fraction of the crystal volume (~0.02%), the total mass of the crystals were used to calculate this contribution. All the experimental magnetisation results presented below already include this correction.

In Figure 3 the temperature dependence of magnetisation for the three implanted oxides is shown. The curves display the common feature of an approximately constant magnetisation value up to 380 K, suggesting a Curie temperature well above room temperature. The hysteresis loops measured for the same samples at 300 K (Figure 4) confirm the existence of ferromagnetism at this temperature.
In order to check for the existence of impurities particle induced X-ray emission (PIXE) was performed on the samples. In the case of TiO$_2$, no impurities have been detected. For the implanted and virgin ZnO crystals emission peaks for various transition metal impurities were observed with a concentration smaller than 0.04 at. % and an estimated contribution to the total magnetic moment between 5 and 50 times smaller than the measured values.

To recover the lattice structure and modify the concentration of defects, the following heat treatments were carried out: for ZnO two consecutive annealings in air at 400ºC and 500ºC for 6 h and for TiO$_2$ one annealing at 800ºC for 1 h in argon atmosphere.

The RBS-C spectra shown in Figure 6 show that prior to the annealing the implanted region is highly damaged in both cases and that the damage induced after implantation is significantly reduced with the thermal treatments, although some disorder still remains. This information is obtained comparing the yield for incident ions along one of the crystalline directions of the crystals with the values of the same yield for the non implanted sample. The high yield observed in the RBS-C, in the implanted depth spectra, after implantation almost equals the yield obtained for a non aligned direction indicating a highly disordered region. After annealing this yield decreases in a large depth.

The magnetization results after the heat treatments are presented in Figure 7 for Ar implanted ZnO and TiO$_2$. The results show that the process of recrystallization and lattice recovery induced by the annealing is accompanied by a reduction or disappearance of the ferromagnetic signal, respectively for TiO$_2$ and ZnO in the case of the thermal treatments referred.

![Figure 6. RBS-C spectra for TiO2 implanted with argon.](image)

![Figure 7. Comparison between hysteresis curves obtained, before and after the thermal treatment, for samples implanted with 1×10$^{17}$ Ar cm$^{-2}$.](image)
Given the low impurity concentration, the formation of aggregates with nanosize dimensions induced by the implantation procedure could be put forward to explain the observed magnetic signal in ZnO. However, such nanosized particles would have superparamagnetic behaviour and no evidence of such behaviour can be found neither for the virgin or the implanted crystals (Figure 3).

In order to understand further the mechanism behind the appearance of the magnetic moment, band structure calculations using density functional theory within the generalised gradient approximation were performed for ZnO. A supercell of 128 atoms and periodic boundary conditions were used. Two types of defects, Zn vacancies and oxygen vacancies, were considered the calculated values of the associated moments being 1.05 and 0 $\mu_B$ respectively. For the case of Zn vacancies the magnetic moment results from the polarisation of the oxygen p bands giving rise to defect states just above the valence band as shown in Figure 8. The defect state bands cross the Fermi energy resulting in a metallic solution and are fully polarised.

![Figure 8. Partial densities of states for the case of a Zn vacancy. The zero of energy is at Fermi energy.](image)

3. Conclusions
In this work we have shown that oxide semiconductor single crystals implanted with non magnetic Ar ions develop a ferromagnetic signal at room temperature. The results show that the obtained magnetic behaviour can not be assigned to impurities or to the formation of secondary phases or aggregates and is ascribed to the lattice defects induced by the implantation procedure. Band structure calculations performed for ZnO show that point defects can give rise to polarised bands inside the semiconducting gap, pointing to a possible mechanism for the long range ordering of the magnetic moments. Further experiments and calculations are under progress.

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References
[1] Dietl T, Ohno H, Matsukura F, Cibert J and Ferrand D 2000 Science 287 1019
[2] Pinto J.V., Cruz M.M., da Silva R.C., Franco N., Casaca A., Alves E., and Godinho M., 2007 Eur. Phys. J. B 55 253
[3] Borges R P, Pinto J V, da Silva R C, Gonçalves A P, Cruz M M and Godinho M 2007 J. Magn. Magn. Mater. 316 e191
International Conference On Superconductivity and Magnetism (ICSM2008)
Journal of Physics: Conference Series 153 (2009) 012044
doi:10.1088/1742-6596/153/1/012044

[4] Coey J M D, Venkatesan M, Stamenov P, Fitzgerald C B and Dorneles L S 2005 Phys. Rev. B 72 024450
[5] Young D P, Hall D, Torelli M E, Fisk Z, Sarrao J L, Thompson J D, Ott H R, Oseroff S B, Goodrich R G and
Zysler R 1999 Nature 397 412
[6] Elfimov I S, Yunoki S and Sawatzky G 2002 Phys. Rev. Lett. 89 216403
[7] Chaitania Das P and Sanvito S 2005 Phys. Rev. Lett. 94 217205
[8] Hong N H, Sakai J and Briz‘e V 2007 J. Phys.: Condens. Matter 19 036219
[9] Borges R P et al 2007 J. Phys.: Condens. Matter 19 476207
[10] Garcia M A et al 2007 Nano Lett. 7 1489
[11] CRC Handbook of Chemistry and Physics 1999 80th edn (Boca Raton, FL: CRC Press) p 4-134
[12] Janisch R, Gopal P and Spaldin N A 2005 J. Phys.: Condens. Matter 17 R657