Room-temperature Ferromagnetism in Ion-implanted Co-doped TiO$_2$(110) Rutile


B.S. Mun, N. Hamdan, and P. Nachimuthu, Advanced Light Source, Lawrence Berkeley National Laboratory, Berkeley, CA 54720 USA

B.Taylor, R. P. Sears, and B. Sinkovic, Department of Physics, University of Connecticut, Storrs, CT 06269 USA

**Introduction**

Practical spintronic devices will require room temperature magnetic semiconductors. Previously it has been demonstrated that Co doped anatase is a robust room temperature semiconductor[1]. Another approach to producing magnetically doped semiconductors is by ion implantation. In this work we show that ferromagnetic behavior is found for Co implanted into the related TiO$_2$ material, rutile[2]. No metallic Co is observed, but some second phase CoO is found. Taking this second phase into account, the net magnetization for the Co in rutile is 0.6 µB/atom.

**Methods and Materials**

Single-crystal rutile TiO$_2$(110) substrates were purchased from Princeton Scientific Corporation and were implanted with 100 keV Co$^+$ ions at Implant Sciences Corporation at a substrate temperature of 1075 K and an ion fluence of $2.5\times10^{16}$ ions/cm$^2$. Following implantation, the samples were characterized by vibrating sample magnetometry (VSM) and the magneto-optical Kerr effect (MOKE) to determine the magnetic properties. Also, the structural and compositional properties were determined by Rutherford backscattering spectrometry (RBS), x-ray photoelectron spectroscopy (XPS) depth profiling and x-ray diffraction (XRD). Co K-edge XANES and extended x-ray absorption fine structure (EXAFS) measurements were made at the Argonne Advanced Photon Source using the PNC-CAT beamline 20-ID for parallel ($s$ polarization) and perpendicular ($p$ polarization) orientation of the electric field vector relative to the surface, respectively. For both measurements the sample surface made an angle of ~1° with respect to the beam direction and to reduce Bragg peak artifacts the samples were spun about the surface normal.

**Results**

A typical VSM hysteresis loop taken at room-temperature from a Co-implanted TiO$_2$(110) rutile sample is shown in Fig. 1. The magnetic field was oriented perpendicular to the sample surface. However, there were no noticeable differences between in-plane and perpendicular magnetization loops. The sample shows clear ferromagnetic behavior with a saturation magnetization of ~0.4 µB/Co atom, assuming that all the Co atoms contribute to the magnetization. This value is considerably less than that of pure Co metal (1.7 µB /Co atom), and that found for Co-doped TiO$_2$ anatase grown by molecular beam epitaxy (~1.2 µB /Co atom). It is also less than that reported for Co-doped rutile TiO$_2$ films (~1 µB /Co atom)[3,4]. The coercive field was found to be ~100 Oe with a remanence of ~20%.

![Fig. 1 Room-temperature VSM hysteresis loop for ~2 at. % Co-implanted TiO$_2$ (110) rutile. The substrate temperature was 1075 K during implantation.](image)

Co K-edge measurements can be used to verify that the magnetic signal is not due to metallic nanoparticles. These results are show in Fig. 2, where the near edges of various Co compounds are compared. It is clearly established that all of the Co is in the Co(2+) charge state. Comparison with the standards suggests that some CoO second phase may be forming. Fig. 2b shows a fit to the data using a linear combination of the three standards. The best fit gave 0% Co metal, 64% Co in anatase, and 36% CoO.

Since the near edges of various Co(2+) compounds can be similar, a better way to look for CoO is by analysis of the EXAFS. Fig. 3 shows the Fourier transformed EXAFS spectrum compared to two multishell fits. One fit uses a substitutional model of Co in rutile, while the other fit also includes a component for CoO. CoO has a strong signal from the second shell Co-Co distance that cannot be fit with the simple substitutional model. This fit gave 66% Co in rutile and 34% CoO, in excellent agreement with the near edge fit. This fitting also gives more information about the Co site. The nearest neighbor Co-O distance for the Co in rutile component was found to be 2.01 Å. This is similar to the Co site in Co doped anatase[1].
Discussion

In determining the moment per Co, it was assumed that all the Co atoms contribute to the magnetization. Based on the results discussed above from XANES, EXAFS and XRD, it appears that ~1/3 of the implanted Co is present as a CoO secondary phase. Since CoO is anti-ferromagnetic in the bulk, only ~2/3 of the Co atoms contribute to the ferromagnetic response of the implanted sample. Although nanoscale CoO particles may contribute to the net magnetization due to canted moments on the surface\cite{5,6], we have not included this possibility in our analysis. Thus, the magnetic moment per magnetically active Co is ~0.6 $\mu_B$/Co atom.

In summary, we have successfully synthesized ferromagnetic rutile TiO$_2$ single crystals by high temperature Co ion implantation. VSM measurements reveal clear ferromagnetic behavior at room temperature, with an effective saturation magnetization of ~0.6 $\mu_B$/Co atom. Co is in the +2 formal oxidation state throughout the implanted region. There is no evidence for metal Co(0).

Acknowledgements

This work was supported by the Laboratory Directed Research and Development (LDRD) at Pacific Northwest National Laboratory (PNNL), which is operated by Battelle for the DOE under Contract No. DE-AC06-76RLO-1830. Much of the characterization was conducted at the Environmental Molecular Sciences Laboratory (EMSL) funded by the DOE Office of Biological and Environmental Research (OBER). PNC-CAT facilities and research at these facilities is supported by the US DOE Office of Science grant no. DE-FG03-97ER45628. Use of the Advanced Photon Source was supported by the U.S. DOE, under Contract No. W-31-109-ENG-38.