Room-temperature Ferromagnetism in Ion-implanted Co-doped TiO_2(110) Rutile

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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 μ_B /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 $2.5x10^{16}$ 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 $_B$/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 μ_B /Co atom), and that found for Co-doped TiO_2 anatase grown by molecular beam epitaxy (~1.2 μ_B /Co atom). It is also less than that reported for Co-doped rutile TiO_2 films (~1 μ_B /Co atom)[3,4]. The coercive field was found to be ~100 Oe with a remanence of ~20%.

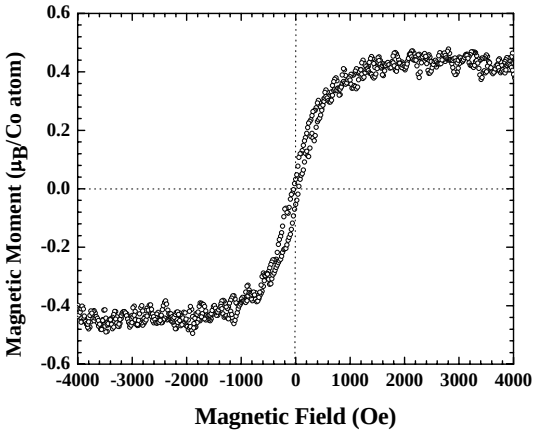

Fig. 1 Room-temperature VSM hysteresis loop for ~2 at. % Co-implanted TiO_2 (110) rutile. The substrate temperature was 1075 K during implantation.

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].

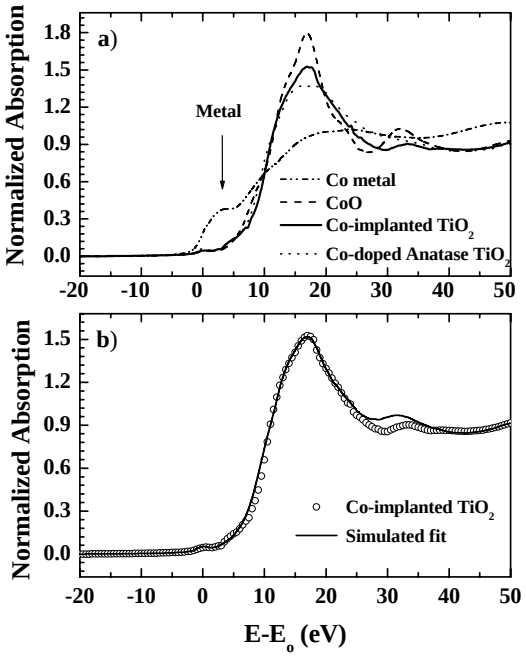

Fig. 2. (a) Co K-edge XANES spectra from Co metal, CoO, $CoTiO_3$, and Co-implanted rutile TiO_2. (b) Co K-edge XANES spectra (open circles), along with a simulation consisting of a weighted average of Co spectra from various reference materials (solid line). The weighting factors for the optimized fit are 0 for Co metal, 0.36 for CoO and 0.64 for $CoTiO_3$.

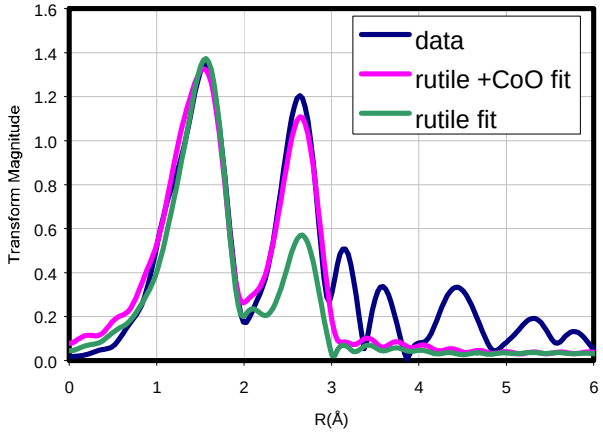

Fig. 3. Measured (open circles) and simulated radial distribution functions for Co K-Edge EXAFS data from Co-implanted TiO_2 rutile with: (1) a substitutional-Co-in-rutile model (dashed line), and (2) a Co-in-rutile (34 ± 4%) plus CoO (66 ± 4%) model (solid line). The transforms are k^2 weighted and taken over the range 2-11 $Å^{-1}$. The fitting was carried out over the range of 1-3 Å.

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 is 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[5,6], we have not included this possibility in our analysis. Thus, the magnetic moment per magnetically active Co is ~0.6 μ_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 μ_B/Co atom. Co is in the +2 formal oxidation state throughout the implanted region. There is no evidence for metal Co(0).

Acknowledgements

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