Epitaxial Growth and Properties of Nanoscale Oxides for Spintronics

Scott A. Chambers, Timothy C. Droubay *FY 2003 Cost: $401.9K*

◆ An exceedingly important class of materials required for the realization of advances in spin-based electronics is that of ferromagnetic semiconductors that retain their magnetism at and above room temperature. We have synthesized, characterized, and are starting to understand the most thermally robust, magnetically strong class of itinerant ferromagnetic semiconductors ever reported. ◆

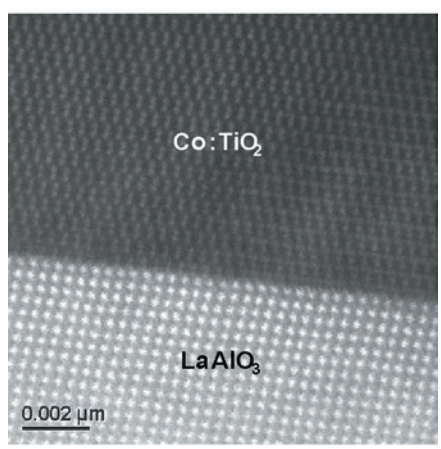
The aim of this project is the exploratory search for new, unconventional magnetic oxide semiconductors that may be useful in the rapidly emerging field of spintronics. Spintronics represents a potentially revolutionary new way to do computing and signal processing. If successful, spintronics not only will allow us to process information orders of magnitude faster and more energy efficiently on circuits that are orders of magnitude smaller than what we currently have with solid-state electronics but will also make possible entirely new functionalities. However, spintronics will remain a concept until suitable materials can be developed, understood, and integrated into useful device structures. Of particular interest is the discovery of semiconducting materials with magnetic ordering temperatures that are higher than those of conventional ferromagnetic semiconductors, which are typically nonmagnetic above ~100 kelvin. Our goal is to synthesize and characterize novel materials in thin-film form and then explore the properties of these materials when they are fashioned at the nanoscale.

In the first and second years of this project, we discovered that cobalt-doped anatase, grown by oxygen plasma-assisted molecular beam epitaxy, is a robust diluted magnetic semiconductor (DMS) with a magnetic ordering temperature (Curie point) in excess of 700 kelvin, the highest of any known DMS. So far, our efforts have centered on growing this unique material as thin (tens of nanometers) single-crystalline films on strontium titanate and lanthanum aluminate, and exploring its structural, electronic, and magnetic properties. We found that despite our best efforts to grow single-phase epitaxial films, we invariably end up with nanoscale particles of either anatase or rutile (depending on the exact growth conditions) embedded in a matrix of single-crystal anatase. The overall density and size distribution of these particles depends on growth conditions, with the smallest and least dense particles accompanying the slowest growth. Moreover, there is some tendency for the cobalt to segregate in these nanoscale particles to an extent that also depends on the precise growth conditions. In FY 2003, our goal was to more fully characterize the nucleation and growth, and electronic and magnetic properties of these fascinating and potentially useful materials, and to extend the investigation to include iron as the magnetic dopant.

In FY 2003, we synthesized and characterized several new materials in addition to further exploring the properties of cobalt-doped TiO_2 anatase. The new materials include cobalt-doped ZnO, iron-doped TiO_2 rutile, and chronium-doped TiO_2 rutile and anatase. We have grown epitaxial $Co_xZn_{1-x}O$ films on $Al_2O_3(012)$ substrates by metalorganic chemical vapor deposition using a liquid precursor delivery system. High concentrations of cobalt ($x \leq 0.35$) can be uniformly incorporated into the film without phase segregation. Cobalt is found to be in the +2 oxidation state, independent of x. This material can be grown *n*-type by the deliberate incorporation of oxygen vacancies, but not by inclusion of ~1 at. % aluminum. Semiconducting films remain ferromagnetic up to 350 kelvin. In contrast, films without oxygen vacancies are insulating and nonmagnetic, suggesting that exchange interaction is mediated by itinerant carriers. The saturation and remanent magnetization on a per cobalt basis was very small ($< 0.1\ \mu_B$/Co), even in the best films. The dependence of saturation magnetization, as measured by optical magnetic circular dichroism, on magnetic field and temperature, agrees with the theoretical Brillouin function, demonstrating that the majority of the Co(II) ions behave as magnetically isolated S = 3/2 spins.

We have also grown epitaxial iron-doped TiO_2 rutile films on rutile $TiO_2(110)$ substrates by oxygen-plasma-assisted molecular beam epitaxy, and have explored the resulting compositional, structural, morphological, and magnetic properties. Clusters of mixed TiO_2 rutile and Fe_3O_4 form on the surface of a continuous rutile epitaxial film during growth. Room temperature ferromagnetism is observed, but is associated with the formation of secondary phase Fe_3O_4 rather than a true diluted magnetic oxide semiconductor.

This work provided the scientific underpinnings and technological methods required for the growth of oxide-based heteostructures that incorporate magnetic semiconducting layers with Curie temperatures at or above room temperature. The availability of such materials systems enables the fabrication of the essential device elements required for a mature spintronics technology to evolve.



Scanning transmission electron micrograph of epitaxial Co-doped TiO_2 on $LaAlO_3(001)$.