Ferromagnetic Cr-doped ZnO for spin electronics via magnetron sputtering

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Through nonequilibrium rf magnetron cosputtering of ZnO and Cr metal on a-plane Al_2O_3 we find ferromagnetic ordering with a room-temperature saturation moment of $1.4\mu_B$ per Cr ion at a doping concentration of ~ 9.5 at. % after UHV postanneal. No secondary phases are detected in the films via x-ray diffraction (XRD). Increased Cr doping causes disorder within the films resulting in decreased overall, and per Cr, moment. The Curie temperature exceeds 365 K, the maximum temperature reached in our experiment. All films are dielectric with a resistivity higher than 10^6 Ω cm at room temperature. The lack of carriers indicates that the ferromagnetic mechanism is not carrier mediated. © *2005 American Institute of Physics*. [DOI: 10.1063/1.1847914]

Oxide diluted magnetic semiconductors (DMSs) have recently been of intense focus as a subset of the field of spin electronics[1] primarily due to the observed Curie temperatures exceeding room temperature. These observations are in agreement with the theoretical predictions for several wide-band-gap DMS materials.[2] Their large band gaps also make them mostly transparent. AlN, GaN, GaP, TiO_2, ZnO, SnO_2, and others have been considered as candidate host materials for DMS in spintronic applications with varying success.[1] The cause of ferromagnetism in doped oxide materials is still undetermined[3] with several candidate mechanisms including double exchange,[4] carrier-mediated Ruderman–Kittel–Kasuya–Yosida [RKKY-type] coupling,[2] super exchange,[2] and the most recently proposed F-center exchange.[5] ZnO has been of primary interest as a DMS since Dietl *et al.*[2] predicted a Curie temperature greater than 300 K for Mn-doped, p-type ZnO in 2000, and a subsequent experimental finding of Co-doped n-type ZnO was published in 2001 by Ueda *et al.*[6] Recent work has resulted in transition-metal dopants achieving ferromagnetism in n-type ZnO (Mn, Co, Ni, V, and Fe dopants).[6–10] Wurtzite ZnO is commonly used in optical applications as it has a wide band gap of 3.2 eV, making it transparent, and has a large exciton binding energy of 60 meV.[11] ZnO is typically n type, and its electron concentration can be greatly improved by doping with Al, Ga, or In. A p-type ZnO has proven difficult,[12] requiring controlled nitrogen deposition conditions and gallium doping,[13,14] although activated phosphorus by rapid thermal anneal[15] also appears to produce p-type ZnO with no independent confirmation reported by the time of writing.[11]

First-principle calculations[16,17] indicate that the ferromagnetic state of ZnO:Cr would be more stable than a spin-glass state. The ferromagnetic state in Cr-doped ZnO would also be more energetically favorable than that in Co-doped ZnO. However, ZnO doped with chromium has received little experimental attention, in spite of the similar atomic radii of Zn^{2+}(74pm) and Cr^{2+}(73pm), favorable for doping, and the large moment of $Cr^{2+}(4\mu_B)$. The few initial reports were negative.[6] Reference 18 reports a ferromagnetic sample based on remanent magnetization, but a lack of structural characterization of the material allows the possibility for ferromagnetism to have arisen from an unidentified oxide phase. Ferromagnetic ZnO:Cr was also found when codoped with Li, but the magnetic contribution from $ZnCr_2O_4$ has not been ruled out.[19]

In this paper we investigate the magnetic response of cosputtered ZnO doped with chromium. The primary goal centers on achieving a maximum spontaneous moment per Cr atom in a thin film, which was $1.4\mu_B$ at 9.5% at room temperature, with no indication of secondary magnetic phases. We find ferromagnetism that improves with ultrahigh vacuum annealing, while magnetization and structure degrade with increasing doping over 9.5%. The films are dielectric with resistance per square exceeding 10^{11} Ω, with no change discernable upon annealing due to instrumental limitations.

Growth occurred in a high-vacuum magnetron sputtering deposition chamber through the cosputtering method with a minimum base pressure of $\sim 5 \times 10^{-7}$ Torr and deposited in an Ar atmosphere of 5×10^{-3} Torr. ZnO was deposited from a bulk target, prepared by standard ceramic techniques, with a rf power supply at a rate of 0.15 Å/s at 25 W. Cr was deposited from a metal target with the rf power adjusted to control doping concentration. Films were grown at various nominal substrate temperatures of $250–550\pm50$ °C on a-plane $Al_2O_3(11\bar{2}0)$ substrates. Film thickness varied in the
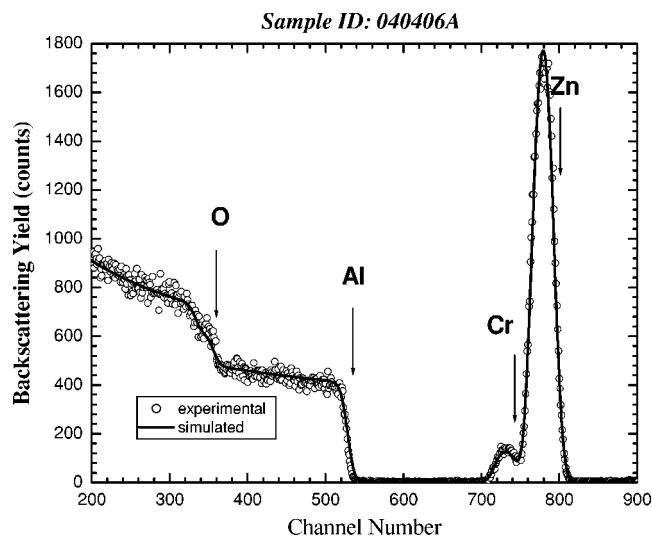
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FIG. 1. Rutherford backscattering channeling data showing ZnO film with 9.5 at. % Cr. The symbols are from experimental measurements; the line results from the simulation of doped film on sapphire substrate.

FIG. 2. Theta–2Theta diffraction patterns of $ZnO:Cr(9.5\%)$ after two annealing treatments at $T=600\ ^\circ C$ in ultrahigh vacuum showing no change in ZnO structure and orientation or additional phase creation. ZnO samples were grown on sapphire substrates and measured with a Si sample holder resulting in several background peaks. Plots for as-grown and annealed samples have been offset for clarity and are otherwise nearly exactly the same.

50–70-nm range. Magnetic characterization was performed on a Quantum Design MPMS-5 superconducting quantum interference device (SQUID) in the temperature range 5 to 365 K and fields of up to 0.5 T. A Rigaku x-ray diffractometer (XRD) with rotating anode and Cu $K_\alpha(\lambda=1.54\ Å)$ radiation was used for x-ray reflectivity to measure thickness and 2θ–θ scans for crystal structure. Rutherford backscattering (RBS) and proton-induced x-ray emission (PIXIE), as well as energy dispersive spectroscopy (EDS) were performed to determine the composition. Some films were annealed in an ultrahigh vacuum chamber at 10^{-9} Torr, where the samples were shielded from errant evaporation from the heating lamp by Si shields. The sample temperature at anneal was roughly 600 °C. A typical annealing treatment occurred with a ramp up for 45 min, hold for 1 h, and cooled in vacuum.

Wurtzite ZnO growth on *a*-sapphire via sputtering occurred best at substrate temperatures of >480 °C. Increasing Cr concentration above 9.5% or increased ZnO deposition rate above 0.3 Å/s shows a trend towards polycrystalline ZnO or amorphous films. All experimental results shown in this paper are for samples with composition $Cr_{0.095}Zn_{0.905}O$ as determined by RBS (Fig. 1) and confirmed by EDS. Figure 1 shows the experimental result of RBS channeling measurement in symbols, with the solid line representing the simulated result for $Cr_{0.095}Zn_{0.905}O$. Pole figures of this sample composition indicate that the growth is *c*-axis preferential with two orientations at 60°, indicated by six spots in the pole figure. XRD 2θ–θ data in Fig. 2 shows no structural difference between an as-grown sample and samples annealed in ultrahigh vacuum. No anomalous peaks indicating phase formations other than ZnO are found in XRD measurements. We assume that Cr ions disperse throughout the ZnO matrix substituting for Zn, but this assumption awaits definitive confirmation.

Initial magnetic measurements of the as-grown samples indicate that spontaneous moment decreases at doping concentration over 9.5% Cr, both over the entire sample
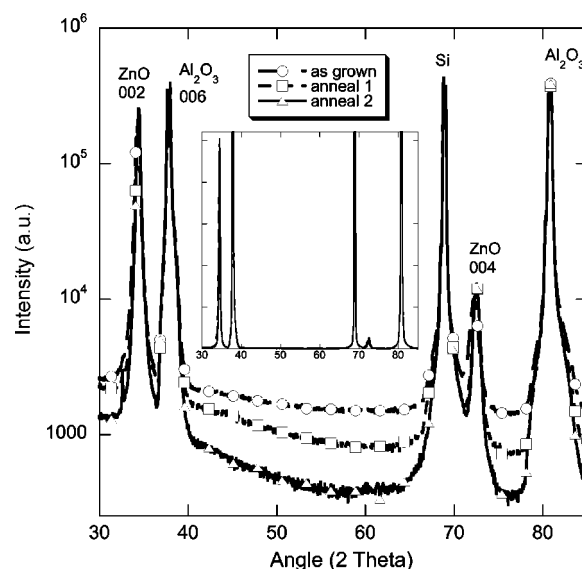
(emu/cc) and per Cr atom. This correlates with deterioration of the crystal quality at increasing concentration. The 9.5% Cr doping sample shows a large saturated moment of ∼$1.2\mu_B$ per Cr atom and open hysteresis loops both at 5 and 300 K prior to anneal (Fig. 3, the diamagnetic substrate signal has been subtracted here). This sample shows sharp ZnO peaks in XRD (Fig. 2) as well. Figure 3 shows an increase in remanent magnetization (M_r), coercive field (H_c) (inset), and saturation magnetization (M_s) (to ∼$1.4\mu_B$/Cr atom) after UHV annealing. To study temperature-dependent magnetic properties, we use measurements of thermomagnetic remanence (TMR) to eliminate the effect of the substrate. Remanent moment is measured in increasing temperature from 5
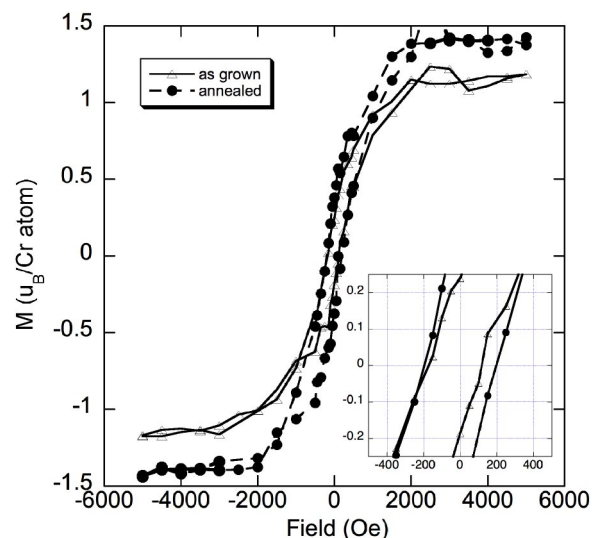

FIG. 3. Hysteresis loops of as-grown and annealed samples showing an increase in M_s, M_r. The inset shows the coercive fields.
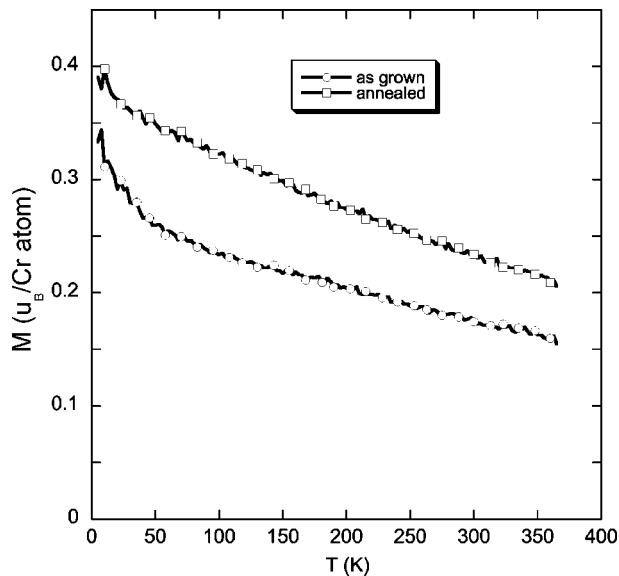
FIG. 4. Thermomagnetic remanence of as-grown and UHV annealed samples showing evidence of remanent magnetization at temperatures exceeding 365 K.

to 365 K after application of external field of 5 kOe and reduction to 0 Oe at 5 K (Fig. 4). It is seen that the Curie temperature exceeds our measurement limit of 365 K. After the annealing treatment at 600 °C, the sample shows improved TMR (Fig. 4) by as much as 35%.

For analyses of the origin of ferromagnetism in Cr:ZnO we need to consider possible magnetic phases in the system. Chromium oxide (CrO_2) is a half-metallic material with Curie temperature of ~ 387 K. A number of antiferromagnetic oxide phases exist but would not contribute to ferromagnetism. If divalent chromium substitutes for Zn in ZnO it will have a moment of $4\mu_B$, while Cr^{4+} ions, such as from CrO_2, have a moment of $2\mu_B$. Our finding of $1.4\mu_B$ per Cr ion is below both theoretical values, and cannot be used as criteria to determine Cr valency. However, taking into account the absence of secondary phases suggested by XRD results, we assume that ferromagnetism can be due to exchange interactions between Cr ions substituting Zn in the lattice rather than from ferromagnetic oxide phases. Measurements to determine oxidation states of Zn and Cr, and the position of the dopant in the unit cell have not been completed at the moment of writing. In order to relate our observations to the existing theories of ferromagnetism in DMS, we measured the resistance of the films with an electrometer. The sheet resistance was above the limitations of the setup ($\sim 10^{11}$ Ω), or resistivity greater than 10^6 Ω cm at room temperature with no measurable difference postanneal. Thus the film is ferromagnetic in the dielectric state, making an application of the theories of carrier-mediated magnetism problematic. This question requires further investigation.

The data presented in this paper show that ZnO can be made ferromagnetic by doping with Cr, though more characterization is needed to determine the Cr valence. No secondary magnetic phases are detected by XRD either. The mechanism of ferromagnetism is not clear but does not appear to be carrier mediated as ferromagnetism is observed in the dielectric films.

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