Effect of hydrogen codoping on magnetic ordering and conductivity in Cr:ZnO thin films

Bradley K. Roberts, Alexandre B. Pakhomov, and Kannan M. Krishnan[a]

Department of Materials Science, University of Washington, Seattle, Washington 98195, USA

We explore the effects of codoping with hydrogen on magnetism, conductivity, and spin polarization of carriers in Cr-doped ZnO. $Zn_{0.99}Cr_{0.01}O:H$ films sputter deposited on sapphire show a correlation between magnetization and conductivity when H is introduced. In the first method, dielectric and weakly magnetic films grown in pure Ar are subsequently annealed at 400 °C in a 5% H_2 95% Ar 1 atm flowing tube furnace. These films show increases in conductivity and saturation and remnant magnetization postanneal. In the second method, conducting ferromagnetic films are grown in the H/Ar mixture. They are magnetic as grown but show a small decrease in saturation and remnant magnetization and conductivity post-H/Ar anneal. Ferromagnetic CrO_2 with $T_C = 390$ K or antiferromagnetic phases are not detected in hydrogenated films. We studied spin polarization of carriers using anomalous Hall effect; however, initial experiments show no such signs, hence spin polarization is not yet confirmed. Hydrogen doped in dielectric Cr:ZnO may contribute to the conductivity and ferromagnetism in a noncausal relationship. © *2008 American Institute of Physics.* [DOI: 10.1063/1.2833843]

Dilute magnetic oxides (DMOs) such as transition-metal-doped ZnO and TiO_2 have been studied extensively as possible candidates for high temperature spintronic materials. Ferromagnetism in these materials is often associated with codoping with either native defects [oxygen vacancies in anatase $Co:TiO_2$,[1] Zn interstitials in Co:ZnO (Ref. 2)] or other elements [for example, Al donor in Co:ZnO (Ref. 3)]. While demonstration of the conditions for high temperature magnetic ordering has been the main achievement in these studies, further progress in this field has been impeded by the lack of decisive evidence of spin polarization of carriers. The latter is the main obstacle for the use of DMOs as semiconductor spintronic materials (dilute magnetic semiconductors or DMSs); moreover, they can be ferromagnetic yet highly insulating. This is why we have even suggested referring to these materials as dilute magnetic dielectrics in some cases.[1] At the same time the search for conditions to obtain DMO-based DMSs is continuing. One promising suggestion in application to ZnO-based DMOs is to use codoping with hydrogen as mediating agent.[4] Experiments on Co:ZnO (Ref. 5) show that indeed the presence of hydrogen leads to enhanced ferromagnetism, while Al donors do not have similar effect. Zinc oxide doped with various transition metals is a well-studied class of material discussed in recent review articles.[6,7] Hydrogen clearly influences the conductivity of ZnO as first reported in Refs. 8 and 9 and is likely the main source of conductivity in otherwise-undoped *n*-type ZnO as a shallow donor whether present as a native defect[10] or artificially introduced.[9] Recent theoretical[11] and experimental[12] studies emphasize the role of oxygen vacancy-hydrogen complexes as shallow donors. One can hypothesize that this complex may play an exchange-mediating role similar to

oxygen vacancies in $Co:TiO_2$,[1] while Ref. 4 considers primarily interstitial hydrogen causing spin-spin interactions between nearest-neighbor transition metal ions.

This work is directed at fabrication of ferromagnetic and conducting Cr:ZnO and studies of possible correlations between conduction and magnetism. So far films doped with Cr have consistently been dielectric in our experiments.[13,14] While the films are ferromagnetic, the key signature of DMS materials is the ability to polarize free carriers. By artificially introducing hydrogen either during growth and/or postannealing processing we are able to significantly improve conductivity and with it, control the magnetism of the samples. However, we have not found spin polarization of carriers in measurements of the anomalous Hall effect (to the accuracy of the experimental setup); hence we assume a noncausal relationship between carriers and magnetism at this stage of our research. Secondary sources of magnetism are always a concern with dilute magnetic materials. No secondary ferro- or antiferromagnetic phases were found in hydrogenated films.

Thin films of thickness ~73 nm were grown via rf magnetron sputter deposition at 45 W in pure Ar and a 5% H_2 95% Ar atmosphere (hereafter referred to as H/Ar) at varying deposition pressures in the range 5–25 mTorr; the base pressure of the chamber was $\sim(1-3) \times 10^{-7}$ Torr. Composite targets were prepared from ZnO and CrO_2 powders via basic ceramic processes with a nominal composition of 1 Cr: 99 Zn. Al_2O_3 in *c*- and *r*-plane orientations and Si with an artificially thick oxide layer were used for substrates; during growth the substrate temperature was 325 °C. Hydrogen annealing at 400 °C was performed using a flowing tube furnace at 1 atm in the same H/Ar gas. Film composition was determined via energy dispersive x-ray spectroscopy, wavelength dispersive spectroscopy, and inductively coupled

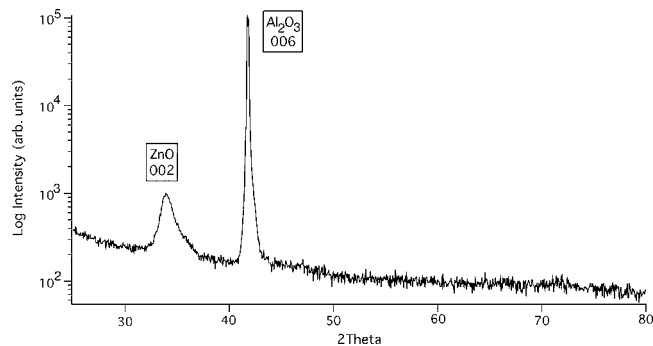[a] FAX: 206-543-3100. Electronic mail: kannanmk@u.washington.edu.

FIG. 1. θ-2θ XRD scan of typical film grown in H/Ar on c-axis Al_2O_3. No secondary phases are detected.
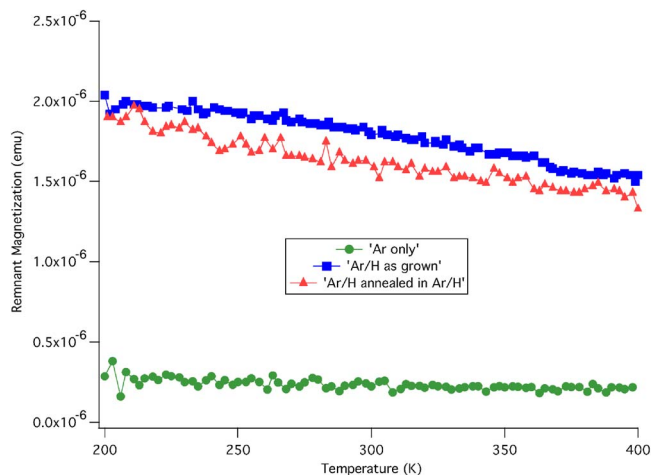

FIG. 2. (Color online) Remnant magnetization of samples grown in pure Ar (green ●) and with artificial hydrogenation during growth H/Ar (blue ■) and postannealing in H/Ar (red ▲).

plasma techniques to be ∼0.9 Cr: 100 Zn. Thickness and orientation were determined by x-ray reflectivity and x-ray diffraction (XRD), respectively. Magnetic properties were determined using a Quantum Design MPMS-5 superconducting quantum interference device magnetometer. Room temperature conductivity was measured via four-point probe method using an Agilent nanovoltmeter and Keithley current source. Hall effect, magnetoresistance, and temperature dependent transport measurements were conducted via van der Pauw method using a Quantum Design PPMS-9 system.

ZnO can be grown on a variety of substrates (including amorphous) resulting in a c-axis oriented film, though to ensure heteroepitaxy it is best to use a sapphire such as r- or c-plane oriented substrate. Use of c-plane sapphire results in an oriented c-axis ZnO film, confirmed via XRD (Fig. 1). Annealing does not appear to alter the structure significantly other than slight peak narrowing, indicating a decrease and relaxation in extended structural defects. Samples grown at the lowest pressures (5 mTorr) show the most ideal ZnO structure, with full width at half maximum increasing with deposition pressure.

The secondary phases are a concern in any diluted magnetic system as a source of spurious magnetic signal. $ZnCr_2O_4$ is an inverse spinel with antiferromagnetic properties to ∼11 K (Ref. 15) and has been detected in other ZnO–Cr publications.[16,17] CrO_2 is metastable in bulk form and is strongly ferromagnetic with a T_C around 390 K.[18] Neither these nor other phases (antiferromagnetic Cr metal, Cr_2O_3, and Cr_3O_4) are detected via XRD though it is possible that such phases exist in volumes below the detection limit. An alternative check for secondary phases involves temperature dependent magnetic measurements (Fig. 2). After a saturation field had been applied and removed, remnant magnetization measurements with temperatures to at least 400 K checked for possible CrO_2. (Remnant measurements rather than saturation moment were performed due to the diamagnetic background of the substrate.) Most samples are ferromagnetic above 390 K, but a few samples grown in pure Ar exhibit a drop in signal at ∼390 K, indicating that some component of the ferromagnetic signal may be CrO_2 like; this drop is always absent following postanneal in H/Ar. In a separate set of measurements, no antiferromagnetic contribution was found below 400 K, precluding Cr metal, Cr_2O_3, or Cr_3O_4 contributions.

Hysteresis measurements (Fig. 3, where diamagnetic background signal has been subtracted) at 300 K show that saturation moments increase nearly five-fold when hydrogen is incorporated versus when grown in pure Ar. Samples grown in H/Ar and subsequently annealed show a slight drop ($0.03\mu_B$/Cr) in saturation moment from the initial value ($0.56\mu_B$/Cr). The magnetic measurements presented in Fig. 2 also show that the Curie temperature well exceeds 400 K, consistent for all hydrogenated samples in this respect. A correlation between the occasional drop at 390 K and processing methods could not be found. The hysteresis data shown in this paper are for samples which do not show this anomaly. The effect of deposition pressure has been studied in the pressure range 5–25 mTorr. As the deposition pressure increased, the magnetic signal decreased until at 25 mTorr, the signal could not be distinguished from noise, however this may reflect primarily the rapid decrease in the deposition rate with increasing pressure and crystal disorder. Low H/Ar deposition pressures (5–6 mTorr H/Ar) result in conductive samples (5 mTorr: 33 Ω cm as grown 140 Ω cm
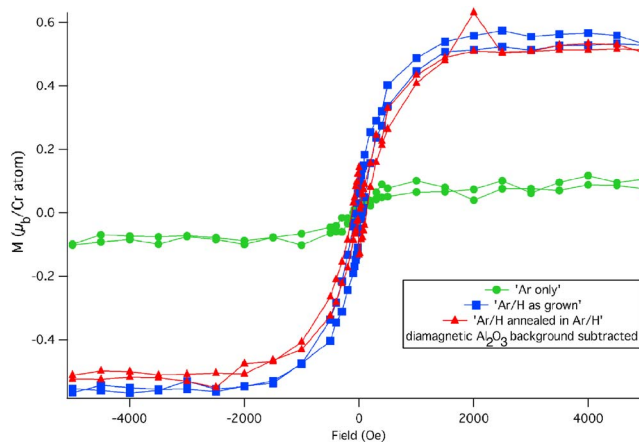

FIG. 3. (Color online) Ar only (●) sample is nonconducting. The sample grown in H/Ar (■) and later annealed in H/Ar (▲) lost a small amount of saturation magnetization and saw a decrease in conductivity and carrier concentration. This trend is consistent with the majority of samples grown in H/Ar.

annealed) while 10 mTorr films measure ~100 s of kΩ cm at 300 K; increasing deposition pressures ultimately result in insulating films at 25 mTorr.

Magnetotransport measurements of the samples have only been obtained for those that have been doped with hydrogen as all samples grown in pure Ar have resistivity >10^6 Ω cm. Hall measurements show no indication of anomalous Hall effect, with a strictly linear response. Based on the ordinary Hall effect, n-type carrier densities are 2.42 $\times 10^{17}$/cm^3 and 1.18×10^{16}/cm^3 at $T=2$ K for the H/Ar grown and annealed samples, respectively. Magnetoresistance of the samples behaves similar to that of ZnO doped with Al and Co,[19] with a change from positive to negative magnetoresistance around 5 K. It has been shown that this behavior is irrelevant to the magnetic doping of the material.[19] After annealing, samples grown in H/Ar show an increase in resistance from tens of percent to several times for the majority of samples, excluding those grown at 25 mTorr which remain insulating. The relative increase in resistance of H/Ar deposited films after annealing shows no apparent correlation with the deposition pressure, nor can a good correlation be determined with the magnitude of change (slight decrease) of saturation moment. We attribute this to the fickle nature of the processing conditions and control of oxygen vacancies and H defects.

Ferromagnetism in this system can be considered with respect to four possible mechanisms. The spin split impurity band exchange model which results in ferromagnetism in transition-metal-doped high-k dielectrics[20] requires that there be overlap between either spin up or spin down transition metal d states and the split donor impurity band, high in the gap at the Fermi level. In ZnO the Cr $3d\uparrow$ levels are within the gap well below the bottom of the conduction band, and $3d\downarrow$ in the conduction band well above the Fermi level, respectively,[20,21] resulting in negligible ordering from this mechanism. The hydrogen mediated spin-spin interaction model (introduced for Co:ZnO in Ref. 4) is short ranged and requires a much higher doping concentration than that reported here. While free-carrier mediated exchange[22] would manifest itself in spin-polarized carriers and hence the presence of anomalous Hall effect,[23,24] which has not been observed yet in our experiments. Based on the current knowledge of the material properties, we would consider as the most applicable a model where magnetism is mediated by defect states above the filled d states of Cr, yet does not assume the band overlap and is independent of the spin polarization of free carriers. A defect-mediated superexchange model of ferromagnetism initially proposed for dilute magnetic dielectrics[25,26] may apply. We show a presence of free carriers lacking spin polarization yet consistent ferromag-

netism, suggesting that there is a noncausal relationship between the two. It is possible that hydrogen occupying an oxygen vacancy (H_O) and creating a multicenter bond shallow donor defect may be responsible,[11,12] both increasing available free carriers and allowing for ferromagnetic superexchange coupling.

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