Surface scaling of magnetism in Cr:ZnO dilute magnetic dielectric thin films

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Measurements of the spontaneous magnetic moment and conductance of oxygen-saturated ZnO:Cr thin films and tunnel junctions show an exponential drop with increasing thickness. All films are in the insulating state. The type and concentration of dominant point defects in the bulk do not provide conditions for magnetic ordering, while surfaces play an important role in magnetism. We suggest that in film thicknesses below a characteristic length (~30 nm), surface states or enhanced concentration of point defects near the surface (oxygen vacancies or incorporated hydrogen) lead to surface magnetism. Ballistic tunneling is observed in junctions <100 nm, with penetration depth of ~10 nm. © *2008 American Institute of Physics*. [DOI: 10.1063/1.2913205]

In certain wide bandgap semiconductors, particularly oxides and nitrides including TiO_2, ZnO, GaN, and AlN doped with magnetic impurities such as Co, Mn, and Cr,[1–3] and classified as "dilute magnetic dielectrics"[4–6] (DMD) or "dilute magnetic insulators,"[7,8] There is evidence of intrinsic bulk ferromagnetism without any dependence on carrier mediation. There is also increasing experimental evidence, primarily for dilute magnetic oxide structures, to suggest that point defects such as oxygen vacancy,[5,6] metal interstitial,[9] hydrogen interstitial,[10] or a multibond hydrogen-in-oxygen-vacancy complex defect[11] can mediate magnetic ordering. However, even though such specific defects have only been identified in very few cases,[12] the particular nature of the pertinent defects and their role in mediating the ferromagnetism is far from being finalized. Although in some cases the defect-mediated magnetism may correlate with conductivity,[9–11] this correlation may be noncausal.[10,11] Extended defects such as twin boundaries may also be involved in magnetic ordering.[13]

Established dilute (ferro)magnetic semiconductors such as GaAs:Mn, best understood in terms of the Dietl model,[14] require spin-polarized free carriers to mediate indirect exchange between the Mn impurities in the Ruderman–Kittel–Kasuya–Yosida–Zener fashion. In DMD, neither the Zener model nor the double exchange mechanism[15] can be applied due to a lack of carriers, while traditional superexchange via *O* or *N* orbitals[16] leads to antiferromagnetism at high concentrations of the magnetic dopant ions.[17] With respect to DMDs, two particularly encouraging mechanisms have been recently proposed in the literature: the bound magnetic polaron (BMP)-based impurity band exchange model[18,19] and the vacancy-state-mediated superexchange model[20,21] which will be referred to as SE.

It has been proposed that DMDs can find applications in spintronic devices as ferromagnetic spin filtering barriers.[5,22] Hence, both ferromagnetic and insulator properties of these materials need to be studied as the film thickness is reduced to several nanometers. This is particularly important since both the BMP and the SE mechanisms might result in the reduction of spontaneous magnetization in thin and ultrathin films, based on the following considerations. In the BMP theory, BMP of shallow donor electrons centered, for example, on oxygen vacancies reach the percolation threshold when the splitting of the impurity band is large, resulting in overlap of the 3*d* band at the Fermi level. Exchange is possible when the donor electron orbitals associated with the polarons overlap creating a three-dimensional (3D) infinite percolation cluster.[23] In the SE theory, the presence of empty defect states in the gap is required for mediation of ferromagnetism, although no carrier motion needs to be involved. According to the original SE model,[21] charge-transfer stabilized defect complexes consisting of oxygen vacancies and magnetic impurities should be of sufficient quantity and interaction radius to exceed the percolation threshold for superexchange in the bulk. Both mechanisms are, thus, dependent on percolation. Assuming uniform and relatively low defect and dopant concentrations, they would both result in a reduction of magnetism at a crossover between 3D and two-dimensional (2D) as the percolation threshold changes from $\sim\frac{1}{3}$ to $\sim\frac{1}{2}$.[23] Our experiments show that an opposite scenario is realized, with *enhancement* of the magnetic moment in thinner films, while the films remain insulating (ballistic tunneling conduction dominant across the thinnest films). These experiments have been performed on samples with low concentrations of the pertinent point defects which allows us to see the enhancement of magnetism more clearly.

We study magnetic properties of insulating oxygen-saturated ZnO doped with Cr as a function of film thickness for a variety of film concentrations and orientations. We find that as the film thickness decreases, the surface ferromagnetism becomes increasingly important. In-plane conductivity of the films is not measurable. Additionally, the thickness dependence of the film conduction measured in the perpendicular direction in tunnel junction-type devices shows that direct ballistic tunneling between electrodes (as opposed to hopping between localized states in the barrier) dominates up to thicknesses on the order of 100 nm, justifying the definition of DMD.

Magnetron sputter deposited $Zn_{1-x}Cr_xO$ films from composite ceramic targets sintered in air (x=1%, 3%, 5%, and 10%) on *c*- and *r*-plane sapphire (following heteroepitaxy, this gives growth of ZnO with *c* axis out of and in plane, respectively) and oxidized silicon substrates (oriented, ZnO

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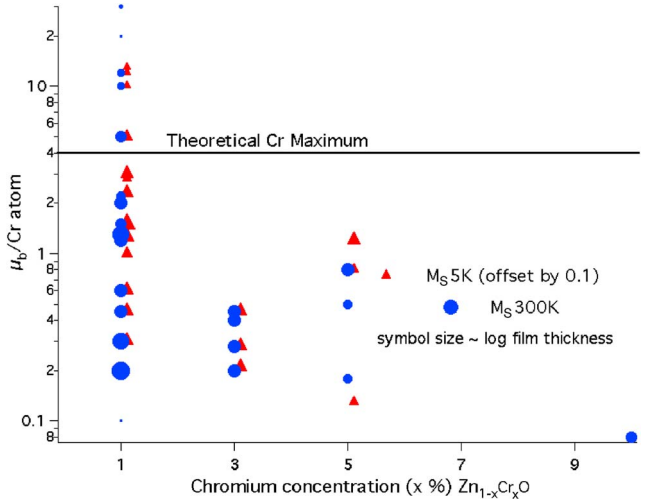

FIG. 1. (Color online) Concentration dependence vs saturation moment for a range of $Zn_{1-x}Cr_xO$ samples. Film thickness is indicated by the symbol size [$\log(t) \sim$ symbol size].

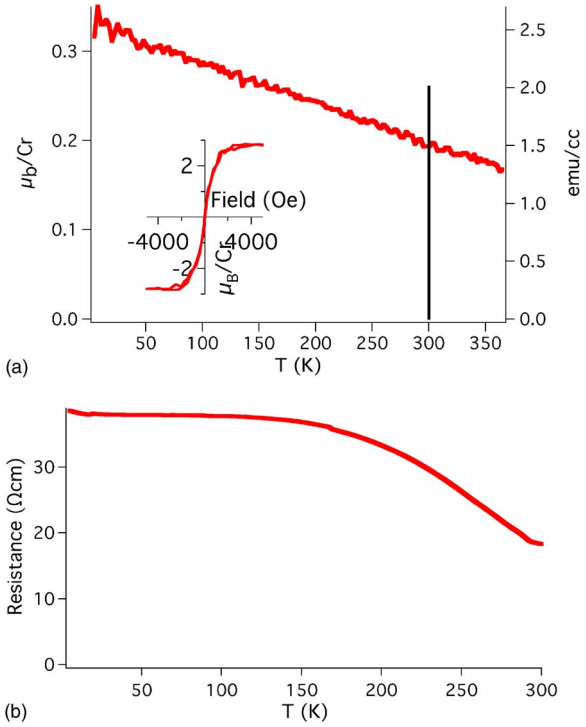

FIG. 2. (Color online) Temperature dependence of thin magnetic film ~50 nm. (a) Remnant magnetization after fully saturating sample. The inset is of background subtracted *M-H* loop at 300 K showing $H_c \sim 80$ Oe. (b) Saturating resistivity of sample indicating ballistic behavior.

c axis out of plane) were prepared at 325 °C in a pure Ar atmosphere at 5×10^{-3} Torr. Structural measurements via x-ray diffraction show no indication of secondary phases such as Cr metal or oxides (including CrO_2 or $ZnCr_2O_4$ as reported in other publications[24,25]). Preliminary positron annihilation experiments on thick films showed no appreciable concentration of oxygen vacancies in the bulk, while Zn vacancy is the dominant point defect.[26] Hence, based on the results of prior reports, one can expect the magnetic properties in the bulk to be weak. Film thicknesses were determined by x-ray reflectivity measurements when possible and calculated from the calibrated deposition rates when necessary (at the smallest and the largest thicknesses where reflectivity oscillations could not be detected). Magnetic properties were measured with a Quantum Design MPMS-5S superconducting quantum interference device magnetometer to 10^{-7} emu sensitivity. Transport measurements perpendicular to the plane of the film were performed on junctions deposited between Au contact layers or Au and Co layers in the cross geometry (junction area 0.2×0.2 mm^2) on artificially oxidized silicon substrates.

Many dilute magnetic (both semiconducting and dielectric) materials show a decrease in per-dopant spontaneous magnetic moment as the concentration of transition metal dopant increases, attributed to antiferromagnetic dopant-dopant interactions at close proximity. Figure 1 shows that our samples exhibit this behavior for a wide range of thicknesses with concentrations varying from 1%–10%. The trend was independent of substrate type and, therefore, film orientation; samples show the same trend regardless of measurement at 5 or 300 K. As the trend was apparent on initial measurements, we mainly focus on samples with 1% Cr. While the theoretical estimate of the magnetic moment for an individual Cr ion is about $4\mu_B$, we find that several samples exceed this limit although this is not uncommon in the literature.[27] In Fig. 1, the symbol size is proportional to the log of the film thickness, with thicknesses ranging from half a monolayer to approximately a micron (near bulk). The thickness dependence is apparent with the trend of thin films showing significantly higher saturation magnetizations when compared to thick films, which are also analyzed below. The variation of magnetization data amongst samples, with the same thickness in this class of materials, is attributed to the sensitivity of their magnetic properties to the preparation conditions.[18] The wide distribution of magnetization data and the observed large moments for some of the thinnest films may be due to large statistical fluctuations of concentrations of dopants and defects in very thin films with low dopant concentrations.

As the films are all either weakly ferromagnetic or very thin, the diamagnetic signal from the substrate overwhelms the ferromagnetic signal; in the case of saturation measurements (*M-H* loops) the diamagnetic background signal is subtracted [inset of Fig. 2(a)]. Alternatively, to completely avoid the diamagnetic background signal, temperature dependent measurements are best performed in zero applied field after a saturation field has been applied in order to acquire the remnant magnetization. All films measured up to 400 K have a remnant magnetic signal with a linear decrease on increasing temperature [Fig. 2(a)]. Experimentally, there is no sharp drop in signal around 390 K, excluding CrO_2 ($T_C \approx 390$ K) as a secondary source of ferromagnetism. The resistance measurements with current perpendicular to plane in thin junctions [Fig. 2(b)] as a function of temperature show typically weak temperature dependence, indicative of ballistic tunneling, although some samples demonstrated hopping-type conductance, especially for thicker samples.

Spontaneous magnetization and conductance of the films rapidly decrease with the film thickness. While an exponential dependence is more apparent in conductance experiments, we use it for both measured parameters. Fitting saturation moments to $M = M_0 \exp[-t/t_0]$ gives the characteristic length t_0 of about 30 nm [Fig. 3(a)]. The perpendicular-to-plane conductances of the devices made of these materials exponentially drop with thickness as expected with tunneling and can be best fit to exponential function $S = S_0 \exp(-t/\lambda)$, where λ (~10 nm) is the effective penetration depth (see

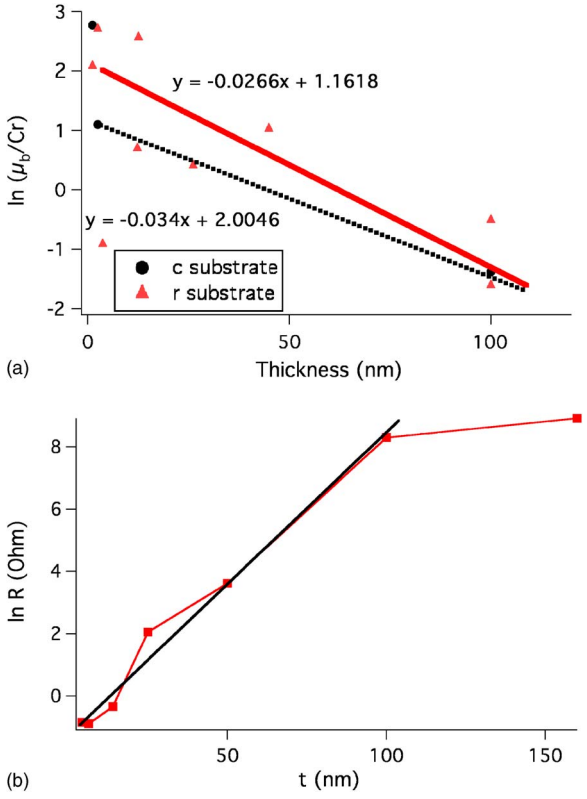

FIG. 3. (Color online) (a) CrZnO saturation moments as a function of thickness. Data to >120 nm not displayed for clarity. (b) Cr:ZnO junction resistance as a function of barrier thickness on a semilogarithmic scale.

Fig. 3(b), where $R=1/S$ is plotted). The difference in the values of the two lengths, 30 nm versus 10 nm, suggests that magnetism and transport are not directly related. Conductivity in device structures with $t<100$ nm is primarily due to ballistic tunneling, although the value of the penetration depth of 10 nm is larger than an estimate, which can be obtained in the Wentzel–Kramers–Brillouin approximation $[2\lambda=(2m/h^2\Phi_B)^{-1/2}]$ based on the barrier height Φ_B. Thus, the material is DMD in the thin film form.

One important result of this work is that Cr-doped ZnO remains a DMD down to the thicknesses of a few nanometers. That is, it is both magnetic and insulating. We have shown before that Cr:ZnO can be made both *magnetic* and *conducting* if it is either deposited or annealed in hydrogen.[11] In the conditions of the present experiment (low concentration of pertinent defects mediating magnetic order), bulk ferromagnetism is weak. However, the magnetic ordering is strongly enhanced in the ultrathin limit, making applications in dielectric spin filtering devices potentially possible. Our results also suggest that percolation-based arguments of either the BMP (Ref. 18) or SE (Ref. 21) models of magnetic exchange fail to describe the behavior of our materials with low concentrations of the pertinent point defects. Contrary to the theoretical expectations, these materials are weakly magnetic to nonmagnetic in 3D but ferromagnetism emerges in quasi-2D films. A plausible interpretation is that the pertinent point defect concentrations near the surface may be different (higher) from that in the bulk. Another attractive possibility is to attribute this type of magnetic ordering to superexchange via surface states. It may be possible to extend the SE model to this case.[28] Experimentally, extended structural defects are known to affect the ferromagnetism of some dilute magnetic oxides.[13] As the surface of a film is one such extended defect, our results are qualitatively in agreement with this work. Notice also that measurements of the bulk forms of otherwise dilute magnetic materials often show significantly decreased or nonexistent ferromagnetic signals compared to their thin film counterparts.[18,29] The surface effects discussed in this work can also explain this controversy.

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