

Ferromagnetism in CuO–ZnO multilayers

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We investigated the magnetic properties of CuO–ZnO heterostructures to elucidate the origin of the ferromagnetic signature in Cu doped ZnO. The CuO and ZnO layer thickness were varied from 15 to 150 nm and from 70 to 350 nm, respectively. Rutherford backscattering experiments showed no significant diffusion of either Cu in ZnO or Zn in CuO layers. Magnetic measurements indicate ferromagnetism at 300 K, which depends on the CuO particle size, but not on the CuO–ZnO interfacial area. Polarized neutron reflectometry measurements show that the observed magnetization cannot be accounted for solely by spins localized near the CuO–ZnO interface or in the CuO layer. © 2008 American Institute of Physics. [DOI: 10.1063/1.2959186]

Since the discovery of room temperature ferromagnetism (RT-FM) in (Zn,Co)O,¹ ZnO has been identified as a promising host semiconductor material for magnetic applications, and has since been shown to exhibit RT-FM when doped with many other transition metal elements, including V, Cr, Fe, Co, and Ni.^{2,3} Remarkably, FM was recently reported in ZnO doped with nonmagnetic Cu ions.^{4,5} However, the origin of the FM in Cu doped ZnO is unclear,⁶ and we have previously⁷ discussed the possible role of CuO planar nanoclusters in promoting a net moment. This is consistent with the suggestion that the puzzling FM in certain diluted magnetic semiconducting (DMS) oxides originate from secondary phase nanocrystals that are crystallographically coherent within the host oxide matrix.⁸ If the concentration of dopant ions exceeds the solubility limit, spinodal decomposition leads to regions with lower and higher densities of magnetic ions.^{8,9} Such mechanisms are believed to be responsible for Co metal clusters in (Zn,Co)O,¹⁰ the ZnMnO metastable phase in (Zn,Mn)O,¹¹ CuO nanoplanar clusters in (Zn,Cu)O,⁷ and the Cr rich (Zn,Cr)Te metallic nanocrystals embedded in a Cr deficient (Zn,Cr)Te matrix.⁹ These secondary phases have traditionally been ruled out as the origin of the FM moment, as they order antiferromagnetically (AFM). However, it has recently been argued that uncompensated spins at the surface of Zn rich CoO,¹² and Co rich (Zn, Co)O,¹³ lead to FM, and that AFM nanoparticles exhibit clear FM signatures. It is important to clarify that how finite-size and surface/interface effects in AFM can lead to FM signals in order to understand the origin of FM in DMS oxides.

In this letter, we report the magnetic properties at the interface of antiferromagnetic CuO and diamagnetic ZnO thin layers by systematically analyzing (i) CuO (150 nm) on sapphire(0001), (ii) [ZnO(350 nm)/CuO(150 nm)/ZnO (350 nm)] trilayer on sapphire (0001), (iii) and ten layers of [CuO(~15 nm)/ZnO(~70 nm)] on sapphire (0001) with the top and bottom layers being ZnO. We find no evidence for diffusion of either Cu into the ZnO layers or of Zn into the CuO layers using Rutherford back scattering (RBS).

The FM magnetization in all samples ranged from 2 to 5 kA/m of CuO. The surface disordered state of the CuO nanoparticles seems to play a major role in determining the FM moment of the samples. Our polarized neutron reflectometry (PNR) measurements suggest that the FM appears to be distributed over a larger region than just the ZnO/CuO interfaces or even just the CuO layers.

We deposited the CuO and CuO–ZnO thin film heterostructures by rf reactive sputtering on (0001) sapphire (α -Al₂O₃) single crystal substrates. Highly pure Zn (99.99%) and Cu (99.999%) targets were used as the sputtering sources for ZnO and CuO, respectively. The samples were sputter deposited in high purity Ar+O₂ atmosphere at a total pressure of 1 mTorr with an optimized oxygen partial pressure of 0.2 mTorr. The first sample we studied was a 150 nm thick pure CuO film. The second sample was prepared by first depositing a 350 nm thick ZnO film on the sapphire substrate, then depositing a 150 nm thick CuO layer on top of this initial film, then finally covering this CuO layer with another 350 nm thick ZnO layer. This three layer ZnO/CuO/ZnO structure will be referred as ZCZ in the following discussion. The third sample was prepared by depositing a ~70 nm thick ZnO layer on sapphire followed by a ~15 nm thick CuO layer. This ZnO(70 nm)/CuO(15 nm) stack was repeated ten times, followed by a final deposition of a 70 nm thick ZnO layer to prepare the multilayer structure. This sample is referred as [ZCZ]₁₀ in the following text. All samples were deposited at 300 K and annealed at 773 K in air after deposition. These three sample geometries were chosen to control the area of the CuO–ZnO interface, while maintaining a fixed amount of CuO and ZnO (for ZCZ and [ZCZ]₁₀) in the different multilayers. The interface between the ZnO and CuO layers is increased by an order of magnitude in the [ZCZ]₁₀ compared to ZCZ.

Figure 1(a) shows the x-ray diffraction (XRD) spectra of the CuO thin film, ZCZ and [ZCZ]₁₀ multilayer heterostructures. The CuO (150 nm) thin films on sapphire are highly textured with (11 $\bar{1}$) planes. Bulk CuO crystallizes in the monoclinic space group *C2/c*.¹⁴ The structure consists of CuO ladders stacked along [110] and [$\bar{1}$ 10] that intersect

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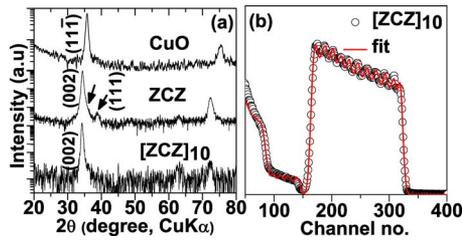


FIG. 1. (Color online) (a) XRD patterns of CuO, ZCZ, and $[ZCZ]_{10}$ samples on sapphire substrate. The arrows show the CuO reflections. (b) RBS spectra of $[ZCZ]_{10}$.

along of $[001]$ by sharing O^{2-} ions. We estimate the particle size to be approximately 14 nm using the Scherrer equation. In ZCZ trilayers additional CuO reflections, $[(111)]$ appear, which indicate more polycrystalline CuO film with randomly orientated grains. The $(11\bar{1})$ reflection (shown by arrow) observed in CuO/sapphire overlaps with the ZnO (002) reflection and is not clearly discernible. The CuO particle size calculated from the resolved component of the $(11\bar{1})$ peak is ~ 8 nm. For the $[ZCZ]_{10}$ sample the CuO peaks are not observed in the XRD pattern and the estimated particle size is much smaller (< 5 nm). The ZnO phase in all samples show only $(00l)$ reflections indicating a texture with basal planes parallel to the substrate area. The appearance of very low intensity (103) reflection at $2\theta \sim 63^\circ$ implies a slight local distortion in the texture, which may be due to interfacial strain at the ZnO–CuO boundaries. Raman spectral studies (not shown) show only peaks consistent with the CuO phase in all samples, with no evidence for a Cu_2O phase. RBS experiments were performed to evaluate the thickness, composition, and interlayer diffusion at the interface. The uncertainty in the thickness of the thick layers is ± 5 nm, while the error in the thickness of the 15 nm layers is ± 2 nm. Figure 1(b) show the typical RBS spectra taken with 0° tilt detector and the theoretical fits for $[ZCZ]_{10}$ heterostructures. No significant diffusion of either Cu in ZnO or Zn in CuO is seen in these films. The RBS spectra for $[ZCZ]_{10}$ were repeated at 30° tilt detectors (not shown) to confirm the absence of diffusion between the ZnO and CuO layers.

Magnetic measurements carried out on a Quantum Design¹⁵ MPMS-5 for the CuO, ZCZ and $[ZCZ]_{10}$ samples are shown in Fig. 2. All the films show well developed magnetic hysteresis at 300 K with a coercivity of approximately 10 mT [Fig. 2(a)]. We measure a FM magnetization (M) of ~ 2 kA/m of CuO for the CuO (150 nm) film on sapphire substrate and ~ 3 kA/m of CuO for ZCZ trilayer. A further

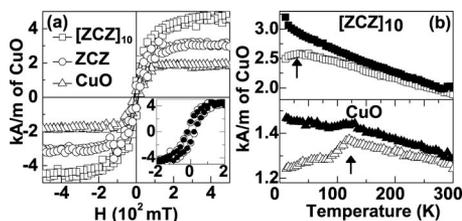


FIG. 2. (a) Hysteresis loops of CuO, ZCZ, and $[ZCZ]_{10}$ samples measured as a function of external applied field at 300 K. (Inset) hysteresis loop measured at 10 K after ZFC (closed circle) and FC (open circle) in 5 T for $[ZCZ]_{10}$. The linear field dependence at high field is subtracted from the data. (b) Magnetization measured as a function of temperature, at magnetic field of 50 mT. The ZFC (open symbols) and FC (filled symbols) were obtained after field cooling the sample from 300 down to 5 K without and with the applied magnetic field, respectively.

slight increase in magnetization, to ~ 5 kA/m of CuO, is observed for the $[ZCZ]_{10}$ heterostructure sample. The presence of FM with a magnetization consistently between 2–5 kA/m of CuO in these widely different samples strongly indicates that the FM is not driven by interlayer diffusion. If the diffusion of metal ions across the ZnO–CuO interlayer boundaries was responsible for the FM we would expect to observe roughly a tenfold increase in the net magnetization between the ZCZ and $[ZCZ]_{10}$ heterostructures, as the latter sample has an interfacial area an order of magnitude larger than the trilayer sample. M versus T measurements after cooling in zero magnetic field (ZFC) and in a finite field (FC) (Fig. 2(b)) shows behavior indicative of superparamagnetism (SPM). In the case of CuO (150 nm) on sapphire the blocking temperature, being approximately indicated by the ZFC/FC separation, is above 300 K. This film also shows an anomaly at ~ 120 K that corresponds to the reduced Néel temperature (T_N) of the small CuO crystallites. Finite-size effects on the magnetic transition temperature in AFM systems studied by Zheng *et al.*¹⁶ show that T_N for CuO nanoparticles decreases with size. The observed T_N of 120 and 25 K for the sample having 14 and ~ 5 nm CuO particles are very close to the values reported in Ref. 16. We also observe SPM behavior in the ZFC-FC dependence of magnetization for the ZCZ and $[ZCZ]_{10}$ heterostructures where the onset of irreversibility falls between 200–250 K. Since the observed FM possibly from uncompensated surface spins could lead to exchange-bias (EB) coupling, we measured the EB effect by carrying out the M - H curve under FC and ZFC conditions. Previous work has shown that interactions between the FM and AFM components in Cu doped ZnO can lead to an EB.⁵ We did not observe any significant EB in the magnetic hysteresis curve measured at 10 K after field cooling the sample in 5 T [Fig. 2(a), inset], suggesting that the exchange coupling in this system is not strong.

In order to determine if the FM originates from a thin ZnO/CuO interdiffusion layer, PNR measurements of the $[ZCZ]_{10}$ sample were carried out using the NG-1 polarized neutron reflectometer at the NIST Center for Neutron Research. PNR is a technique that is sensitive to the structural and magnetic properties of interfaces in multilayer structures.^{17,18} At 300 K, a magnetic field $\mu_0 H = 0.5$ T was applied in the plane of the sample, a neutron beam was spin-polarized alternately spin down ($-$) and spin up ($+$) relative to H , and was incident on the sample. The non-spin-flip (R^- and R^+) specular reflectivities of the sample were measured as a function of reciprocal space scattering vector Q .¹⁹ Model fitting of such scattering can be used to determine the sample's nuclear scattering length density ρ (indicative of the chemical composition) and the component of M parallel to H as functions of depth into the sample.^{17,18} Data fitting was done using the REFLPAK (Ref. 20) and GAREFL (Ref. 21) software packages.

The PNR data and fits generated assuming identical bilayer repeats²² are shown for $[ZCZ]_{10}$ in Fig. 3(a), with the inset summarizing the structural parameters used in the model. The fit is good out to the third order superlattice Bragg position. Evidence of sample magnetization would be manifested as a difference between the R^- and R^+ reflectivities. Since this difference was expected to be small, extra counting time was used to reduce the experimental error bars for measurements at Q close to the first order superlattice

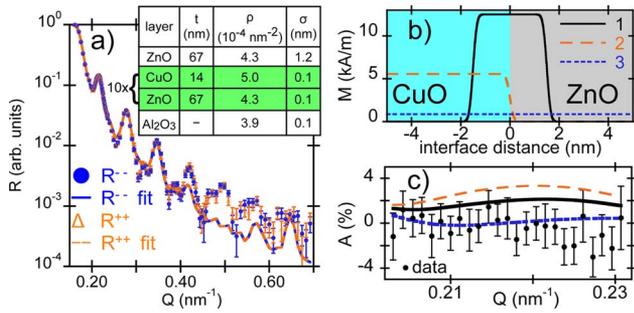


FIG. 3. (Color online) (a) The PNR data and fits for $[\text{ZCZ}]_{10}$. The inset table shows the model parameters: t -thickness; ρ -nuclear scattering length density; σ -roughness. (b) Three different magnetic models: (1) 1.5 nm magnetized on each side of the CuO/ZnO interface, (2) only the CuO layers magnetized, and (3) the entire sample magnetized. (c) The measured spin asymmetry at the first order superlattice Bragg position and calculations corresponding to each of the models in (b).

Bragg position, as the reflectivity signal is high, and calculations suggest that a generic magnetization distribution should produce a relatively large spin-splitting there. However, within experimental uncertainty, we found no spin dependence in the measured reflectivity spectra anywhere in Q , meaning that the distribution of magnetic moments is such that the resulting signal is below our threshold of detection (i.e., consistent with zero magnetization). However, since the total magnetic moment per unit area is known from superconducting quantum interference device (SQUID) magnetometry, the PNR data can be used to rule out possible magnetization depth profiles. Figure 3(b) shows three different distributions of the known total magnetic moment: (1) $M = 12.5 \text{ kA/m}$ only at each ZnO/CuO interface, extending 1.5 nm into each side; (2) $M = 5.6 \text{ kA/m}$ only within the CuO layers; and (3) $M = 0.9 \text{ kA/m}$ throughout the entire ZnO/CuO superlattice structure. The experimental error bars are too large to practically distinguish between these three models except at the first order superlattice Bragg position. Since the spin-splitting is small, it is useful to plot the data as spin asymmetry $A(Q)$, which we define here as the percentage difference between R^{++} and R^{--} . Figure 3(c) shows the measured $A(Q)$ near the first order Bragg peak, and the three calculated $A(Q)$ values corresponding to the magnetic distributions shown in Fig. 3(b). The data are inconsistent both with the interfacial magnetization model (1), and with the model featuring magnetization uniformly localized in the CuO layers (2). Note that models featuring thinner magnetized interfacial layers (not shown) also produce a $A(Q)$ with an amplitude too large to be consistent with the data. However, the data are consistent with a broader distribution of magnetization, for example, one that extends across the entire superlattice structure (3). This suggests that the FM signal observed with SQUID cannot solely be due to narrow interfacial regions, or due solely to a magnetization evenly distributed throughout the CuO layers, and may instead originate from a more homogeneous distribution of magnetic moments. While it seems unlikely that ferromagnetism in the CuO could induce magnetic ordering throughout half the layer thickness ($\sim 35 \text{ nm}$) of diamagnetic ZnO, there are recent reports that pure ZnO can exhibit ferromagnetism, although the origins for this magnetic order remains unclear.²³ However, since a uniform magnetization profile would produce a signal well below the threshold of detection, we are unable to make any affirmative statement concerning the dis-

tribution of the magnetic moments from the PNR measurements.

In summary, we observe magnetizations on the order of 2–5 kA/m of CuO in our thin film heterostructures, approximately independent of the CuO/ZnO interfacial areas. These results strongly indicate that the RT-FM does not arise from CuO–ZnO interlayer diffusion. Additionally, the very small PNR signals observed suggest that the magnetization is not localized at either the CuO/ZnO interfaces, or in the CuO layers. Our magnetic studies point toward the role played by surface disordered spins in promoting FM order. While small CuO particles are known to acquire FM order, which has been attributed to uncompensated spins of the surface Cu ions²⁴ and may provide the basis for the magnetization in the CuO layers. While the microscopic mechanisms giving rise to the FM remain unclear, our measurements unambiguously demonstrate that the magnetization in CuO–ZnO multilayers is not driven by macroscopic interface effects, and does not exist solely in the CuO layers.

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