Enhanced Magnetization of $CuCr_2O_4$ Thin Films by Substrate-Induced Strain

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Abstract

We report the synthesis of epitaxial spinel $CuCr_2O_4$ thin films that display enhanced magnetization in excess of 200% of the bulk values when grown on single-crystal (110) $MgAl_2O_4$ substrates. Bulk $CuCr_2O_4$ is a ferrimagnetic insulator with a net magnetic moment of $0.5\mu_B$ due to its distorted tetragonal unit cell (c/a= 1.29) and frustrated triangular moment configuration. We show that through epitaxial growth and substrate-induced strain, it is possible to tune the magnetic functionality of our films by reducing the tetragonal distortion of the unit cell which effectively decreases the frustration of the magnetic moments allowing for an overall greater net moment.

Complex oxides with spinel structure comprise a family of materials which exhibit a wide range of electronic, magnetic and optical properties through the variation of cations on tetrahedrally and octahedrally coordinated sites. Recently, ferrimagnetic spinel oxides have been identified as spin filter materials for Fe_3O_4 based magnetic junctions[1,2]. Moreover, it has been shown that the isostructural interface between half-metallic Fe_3O_4 electrodes and a spinel barrier layer gives rise to significant junction magnetoresistance that surpass previous rvalues found for Fe_3O_4 based junctions[3]. Of ferrimagnetic spinels, the chromite spinels are of great interest since the strong tendency of Cr cations to occupy the octahedral sites minimizes cation site disorder. Copper chromite is an especially interesting spin filter material due to the dual complexity of its severely distorted tetragonal unit cell and frustrated triangular magnetic moment configuration.

In this paper, we report the first synthesis of epitaxial ferrimagnetic $CuCr_2O_4$ thin films grown epitaxially on (110) and (100) $MgAl_2O_4$ substrates. X-ray diffraction measurements indicate that the films are tetragonally distorted compared to the bulk lattice. Surprisingly, these films have a magnetization of up to 200% greater than bulk and have the potential to exhibit increased spin filtering effects as a barrier layer in magnetic junction structures. This enhanced magnetization is attributed to tetragonal lattice distortions arising from the epitaxial strain induced by the lattice mismatch between the film and substrate. The use of substrate-induced strain to tune magnetic functionality with bulk tetragonal distortions has the potential to be widely applied to complex oxides in technological applications.

$CuCr_2O_4$ (CuCO) is an electrically insulating, magnetic oxide with a room temperature tetragonally distorted (a = b = 6.03Å; c = 7.78 Å; c/a = 1.29) normal spinel crystal structure[4,5]. Figure 1(a) shows a schematic of the bulk tetragonal CuCO unit cell, including a projection of

the (001) plane, and its moment configuration from neutron diffraction studies by Prince[5]. In this projection, we are able to identify the conventional body-centered tetragonal (BCT) unit cell and the face-centered tetragonal (FCT) unit cell which is rotated by approximately 45° relative to the BCT unit cell. We also observe small displacements of the Cr^{3+}cations and O^{2-} anions which, in the bulk, are attributed to the distorting and twisting of flattened CuO_4 tetrahedra about the distorted c-axis[5,6]. Tetragonal distortions commonly occur in the cupric spinels in order to remove the degeneracy of the orbital energy levels due to the d^9 configuration of Cu^{2+} [6]. The severe distortion of CuCO, which has a 20% greater c/a ratio than inverse spinel $CuFe_2O_4$ (c/a = 1.06) is due to the presence of Cr^{3+} and its strong affinity to occupy the octahedral interstitial sites in the spinel crystal[7]. A study of CuCO and $CuFe_2O_4$ (CFO) shows that Cr^{3+} displaces almost all Cu^{2+} from the octahedral sites in CFO, and effectively forces them into the tetrahedral sites[8]. As a result, CuCO is classified as a normal spinel. Furthermore, the distorting and twisting the CuO_4 tetrahedra alter bond lengths affecting the configuration of the magnetic moments since Cr^{3+} - Cu^{2+} interactions no longer dominate over Cr^{3+}-Cr^{3+} or Cu^{2+}-Cu^{2+} interactions as proposed by the Néel model of collinear moments[5,6]. Instead the distortion results in all three interactions being comparable in energy as proposed by Yafet and Kittel[9]. Figure 1(b) illustrates the resultant moment configuration in bulk CuCO, consisting of one Cu^{2+} (1 μ_B) and two Cr^{3+} (3 μ_B) cations arranged in a frustrated triangle. This arrangement leads to a low bulk moment of 0.5 – 0.8 μ_B per formula unit at temperatures below 5K[5,10].

Copper chromium oxide thin films were grown by pulsed laser deposition using a KrF excimer laser (λ= 248 nm) at an energy density of 1.1 J/cm^2 and frequency of 10 Hz. Smooth films with Brillouin-like magnetic temperature transitions were achieved by depositing at 500°C in 15mTorr of O_2. At the completion of the deposition, the films were cooled to ambient temperatures in 100 Torr of O_2.

X-ray diffraction was used to characterize the crystal structure and confirm the epitaxy of our $CuCr_2O_4$ films on (110) and (100) $MgAl_2O_4$ (MAO) substrates. The films ranged in thickness from 45 – 100 nm. Tapping mode atomic force microscopy (AFM) was employed to determined RMS film roughness. Rutherford backscattering spectroscopy confirmed film thickness and stoichiometry. Bulk thin film magnetic measurements were performed using a Quantum Design superconducting quantum interference device (SQUID) magnetometer. X-ray absorption (XA) spectroscopy and x-ray magnetic circular dichroism (XMCD) were performed at BL4.0.2 at the Advanced Light Source to determine cation oxidation states and the relative orientation of the net magnetic moments among the cations.

We have synthesized highly crystalline, smooth CuCO thin films on (100) and (110) MAO substrates. AFM micrographs determined RMS film roughness to be on the order of a unit cell (0.8 nm). Figure 2 shows a typical XRD scan measured in the standard θ - 2θ geometry. This scan exhibits two features which are indexed to the conventional BCT CuCO (400) film peak and the (440) MAO substrate peak indicating a lattice mismatch of 4.4%. The (400) film peak corresponds to an out-of-plane lattice constant of 5.99Å that is approximately 0.63% less than that of bulk (a= 6.03Å). The XRD scans indicate that the tetragonal unit cell (a = b $\neq$ c) of CuCO with b and c in the plane grows epitaxially on top of a 110 oriented cubic

substrate. Assuming a minimization of the in-plane strain, we predict [001]CuCO//[001]MAO and [010]CuCO//[1-10] MAO (Figure 2). This arrangement places the [001]CuCO direction under tension and [010]CuCO under compression and effectively reducing the tetragonality of the unit cell as indicated by a lower c/a ratio.

The temperature dependence of the magnetization measured in a 1T background field is shown in Figure 3. The data indicates that the Curie temperature (T_C) of the films is 125K which is in good agreement with the bulk value of 135K [2,3]. Magnetization versus field measurements of a 47 nm CuCO film grown on (110) MAO resulted in an average magnetic moment of 1.67 μ_B /f.u. at 5K which is a 200% increase over bulk values (0.5 – 0.8μ_B /f.u.). As shown in Figure 4, a 99 nm CuCO film grown on (110) MAO has a smaller magnetic moment of 1.2μ_B /f.u.; however, its magnetization still exceeds bulk by 140%. The decrease in percent enhancement of the magnetization over bulk values for thicker films suggests that the enhanced magnetization is associated with the lattice distortions from epitaxial strain. Finally, XA spectra obtained at the Cu $L_{3,2}$ edges suggest that the oxidation states of Cr^{3+} and Cu^{2+} are preserved in thin film form; while XMCD measurements confirm that these Cr^{3+} and Cu^{2+} cations are magnetic with anti-parallel orientation of the net moments.

The CuCO films display an uniaxial magnetic anisotropy field in the plane of the film. Figure 4 shows that both the out-of-plane $[100]_{BCT}$ direction and in-plane $[010]_{BCT}$ directions represent easy axes while the in-plane $[001]_{BCT}$ direction is magnetically hard. We are unable to measure the in-plane alignment of the film crystal axes by XRD but the strong in-plane uniaxial magnetic anisotropy observed in all CuCO films suggests that the origin of the anisotropy is

associated with either magnetocrystalline or strain anisotropy. In either case, in-plane alignment of the crystal axes would be required to obtain uniaxial magnetic anisotropy.

We propose the origin of the enhanced magnetization to be the reduction in tetragonal distortion induced by the cubic spinel $MgAl_2O_4$ substrates. Epitaxial mismatch between the film and substrate affects the relative orientation of the octahedral Cr^{3+} and tetrahedral Cu^{2+} moments characterized by the angle θ. Based on the triangular moment model in Figure 1(a) and the assumption that Cr^{3+} and Cu^{2+} moments lie in the same plane with minimal out-of-plane rotations of the CrO_6 octahedra, we can calculate θ from the overall net moment found in SQUID magnetometry. We find that a 99 nm thin film has a θ of 68.5°, and a 47 nm film has a smaller θ value of 63.5°. Figure 1(a) shows that θ is 75.5° for bulk CuCO. The reduction of θ results in a greater collinear projection resulting in an increased net moment per formula unit. Compression along the $[100]_{BCT}$ and $[010]_{BCT}$ directions act to "squeeze" the localized Cr^{3+} moments towards a more collinear configuration effectively reducing the frustrated moment configuration of bulk. Thus, the reduction in tetragonality in CuCO thin films as a result of epitaxial growth allows us to manipulate the overall net moment effectively enhancing the magnetization.

In conclusion, for the first time we have synthesized epitaxial CuCO thin films in which we observe an enhanced magnetization that exceeds bulk values in excess of 200%. We postulate that the reduction in tetragonality of the CuCO unit cell due to substrate-induced strain yields a net moment in excess of bulk as a consequence of healing the frustrated moment configuration associated with bulk CuCO. As a result, through careful substrate selection, we are able to manipulate magnetism at the nanoscale via substrate-induced strain effects.

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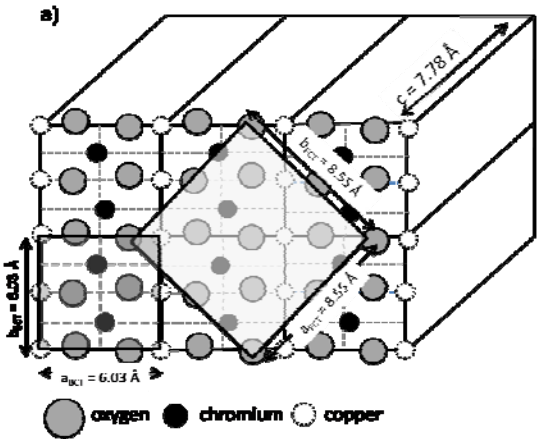
FIGURE CAPTIONS

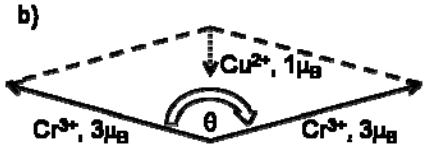
Figure 1 (color online) (a) Schematic of tetragonal CuCO unit cell indicating the atomic arrangement for the (001) plane and corresponding moment configuration. Dark grey (Red) shaded cube represents the conventional body-centered tetragonal unit cell and the light grey (orange) shaded cube represents the equivalent face-centered tetragonal unit cell. (b) Proposed bulk triangular configuration of Cr^{3+} ($3\mu_B$) and Cu^{2+} ($1\mu_{B)}$ moments which yield $0.5\mu_B$/f.u. θ is defined as the relative angle between Cr^{3+} and Cu^{2+} moments.

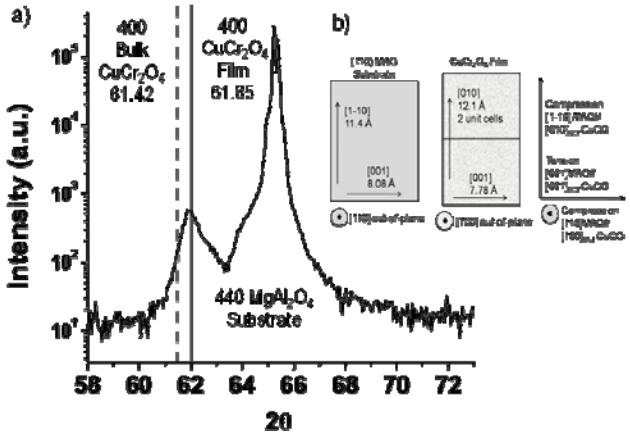
Figure 2. (a) Out-of-plane θ-2θ scan of a 99 nm CuCO film on (110) MAO. Film orientation is indexed to the 400 plane with a corresponding lattice parameter of 5.99Å which is slightly less than that of bulk. (b) Schematic of proposed film CuCO orientation with respect to (110) oriented substrate.

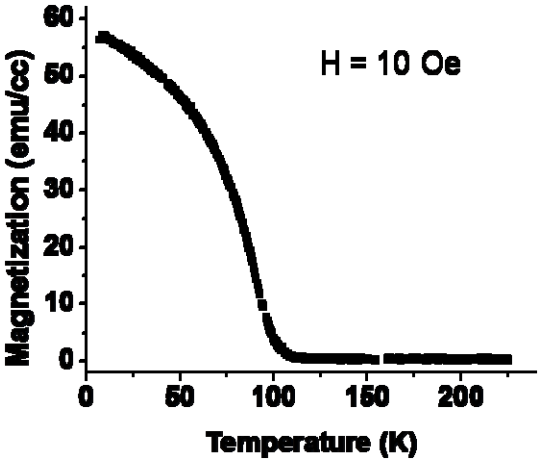
Figure 3. Temperature dependence of the magnetization for a 99 nm CuCO film in an applied field of 10 Oe (OR 1 Tesla??). The T_C of CuCO films is 115K (OR 125K??).

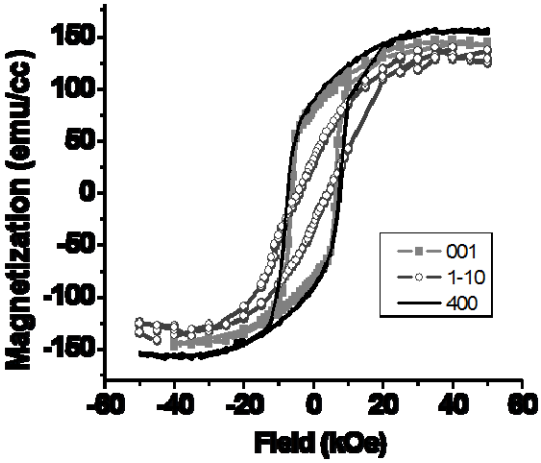
Figure 4. Hysteresis loop for orthogonal directions of a 99 nm CuCO film. We observe in-plane magnetic anisotropy such that the $[100]_{BCT}$ and $[010]_{BCT}$ directions are easy axes while the $[001]_{BCT}$ directions represents a hard direction.

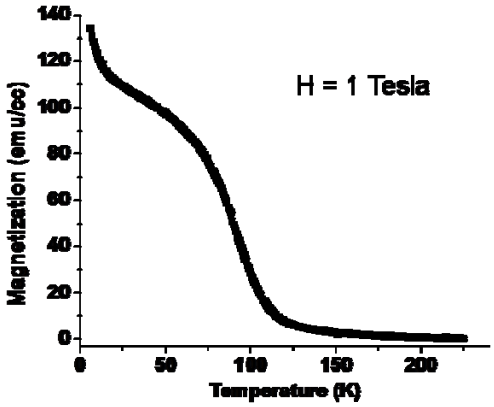

a)
c = 7.78 Å
b_{BCT} = 8.55 Å
a_{BCT} = 8.55 Å
b_{BCT} = 6.03 Å
a_{BCT} = 6.03 Å
oxygen
chromium
copper


b)
Cu^{2+}, $1\mu_B$
θ
Cr^{3+}, $3\mu_B$
Cr^{3+}, $3\mu_B$


a)
400
Bulk
$CuCr_2O_4$
61.42
400
$CuCr_2O_4$
Film
61.85
440 $MgAl_2O_4$
Substrate
Intensity (a.u.)
2θ
b)
[1-10]
11.4 Å
[001]
8.08 Å
[010]
12.1 Å
2 unit cells
[001]
7.78 Å


H = 10 Oe
Magnetization (emu/cc)
Temperature (K)


Magnetization (emu/cc)
Field (kOe)
001
1-10
400


H = 1 Tesla
Magnetization (emu/cc)
Temperature (K)
140
120
100
80
60
40
20
0
0
50
100
150
200