

# Magnetic and structural properties of pulsed laser deposited $\text{CuFe}_2\text{O}_4$ films

Aria Yang

Department of Electrical and Computer Engineering, Northeastern University, Boston, Massachusetts 02115

X. Zuo

Department of Electrical and Computer Engineering, Northeastern University, Boston, Massachusetts 02115 and College of Information Technical Science, Nankai University, Tianjin 300071, China

L. Chen, Z. Chen, C. Vittoria, and V. G. Harris

Department of Electrical and Computer Engineering, Northeastern University, Boston, Massachusetts 02115

(Presented on 11 November 2004; published online 10 May 2005)

Highly crystal textured copper ferrite films have been grown on (100) MgO substrates using pulsed laser deposition. Deposition temperatures were varied from 600–900 °C, with deposition oxygen pressure varied from 1 mTorr to 120 mTorr. Saturation magnetization was measured to increase monotonically with substrate temperature approaching the bulk value of 1700 G near 900 °C. Magnetization was also shown to increase with oxygen pressure with a maximum value of 2481 G obtained at a pressure of 90 mTorr. Although divalent Cu prefers octahedral sites (i.e., 85% under equilibrium conditions), cation inversion was measured to decrease with increasing oxygen pressure and magnetization. © 2005 American Institute of Physics. [DOI: 10.1063/1.1855713]

## I. INTRODUCTION

Spinel ferrites are unique materials that offer low loss performance at high frequencies owing to their high electrical resistivity, high permeability, and high magnetization (albeit for oxide materials). In the spinel structure oxygen atoms form a close packed lattice with transition metal cations residing at the interstices [defined as the tetrahedral (*A*) and octahedral (*B*) sublattices]. The type, valence, and distribution of these cations determine to a large degree the magnetic and electronic properties. Copper ferrite in its bulk equilibrium form is normally a mixed spinel, with  $\approx 85\%$  of the Cu ions occupying the octahedral sublattice.<sup>1</sup> Density functional theory suggests that if the cation distribution can be varied, i.e., increasing the  $\text{Cu}^{2+}$  on the tetrahedral sublattice, the imbalance of spins on the two sublattices coupled with a strong *A-B* exchange will result in a significant increase in the room temperature magnetization. It has been reported that copper ferrite can exist in both cubic and tetragonal structures depending on the thermal treatment used in processing. The tetragonal phase has a *c/a* ratio ranging from 1.01–1.06 with  $a=b \sim 8.35 \text{ \AA}$ .<sup>2</sup> It has been suggested that the degree tetragonal distortion is closely related to cation disorder.<sup>3</sup> This relationship has motivated us to study the nonequilibrium processing of copper ferrite in order to explore the range of cation disorder and the corresponding magnetic properties. Here we report the effects of oxygen pressure and growth temperature on the magnetic and structural properties of  $\text{Cu}$ -ferrite films.

## II. EXPERIMENT

### A. Film processing

Copper ferrite thin films were prepared by pulsed laser deposition (PLD) from a single phase target of  $\text{CuFe}_2\text{O}_4$ . A

total of 8000 laser shots at an energy of 400 mJ per shot resulted in film thicknesses of 300 nm. (It is noteworthy that the film thickness varied with oxygen pressure.) Two processing studies were performed. The first study involved the deposition of a set of films grown at substrate temperatures ranging from 600 °C to 900 °C: the pressure remained fixed at 1 mTorr for all samples. A second study entailed the deposition of a series of films grown at oxygen pressures ranging from 1 to 120 mTorr: the substrate temperature was fixed at 700 °C for all samples. Samples were characterized using x-ray diffraction, vibrating sample magnetometer, ferromagnetic resonance (FMR), atomic force microscopy, and extended x-ray absorption fine structure (EXAFS).

### B. Extended x-ray absorption fine structure

X-ray absorption spectra were collected at the National Synchrotron Light Source using beam line X23B. The design and optical performance of this beam line are described in Ref. 4. Data collection was performed in fluorescence yield at room temperature under standard conditions.<sup>5</sup> EXAFS analysis of cation distribution was first performed by Harris *et al.* in 1996.<sup>6</sup> This approach has been extended by Calvin who in 2002 performed the first multiedge refinement of the spinel structure.<sup>7</sup> Both Harris *et al.* and Calvin *et al.* made use of theoretical standards generated by FEFF codes of Rehr *et al.*<sup>8</sup> together with the refinement procedures outlined by Sayers and Bunker in Ref. 9. In this paper, we applied the multiedge refinement of the spinel ferrite structure using Athena and Artemis codes of Ravel<sup>10</sup> and Newville,<sup>11</sup> respectively, to analyze the distribution of cations in samples produced under varying processing conditions.

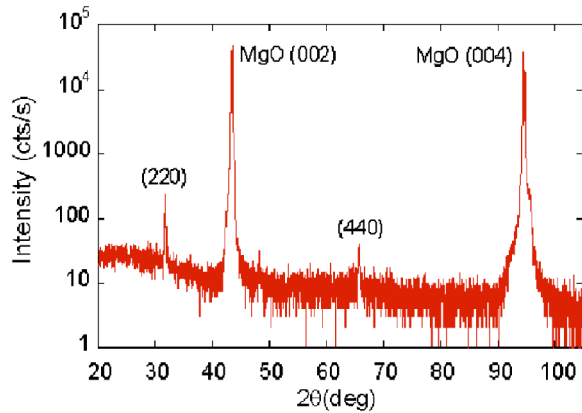


FIG. 1.  $\theta$ - $2\theta$  x-ray diffraction pattern for the sample grown at 1 mTorr of oxygen pressure and a substrate temperature of 700 °C. The (022) and (044) diffraction peaks correspond to the  $\text{CuFe}_2\text{O}_4$  phase.

### III. RESULTS AND DISCUSSIONS

#### A. Processing, structure, and morphology

Figure 1 is a  $\theta$ - $2\theta$  plot of x-ray diffraction data collected from a sample grown at 1 mTorr and 700 °C. We observe in Fig. 1 a high degree of crystal texture where only  $(n,n,0)$  diffraction peaks are present. Atomic force microscopy images and surface roughness data are presented in Fig. 2. As a function of substrate temperature, we find that large cubic crystals ( $\sim 400$  nm on a side) occur in the sample grown at 700 °C (1 mT) having a corresponding minimum surface roughness of  $\sim 5.3$  nm. This corresponds with a high degree of crystal texture [see Fig. 1(a)]. At higher temperatures, the grains appear larger but in fact have a substructure of smaller grains. This corresponds to an increased roughness greater than 10 nm. FMR measurements of the samples prepared at 600 °C and 900 °C illustrate two distinct mainlines suggesting that the samples may have multiple magnetic phases. FMR measurement of the 700 °C processed sample has a single FMR mainline. For these reasons we decided to use 700 °C as the substrate temperature for the oxygen pressure study. In this same figure, we note that the surface roughness as a function of oxygen pressure reaches a minimum of  $<1$  nm at 60 mTorr and increases at higher and lower pressures. The image of the 60 mTorr processed sample is virtually featureless due to the lack of surface roughness. The characterization of the atomic structure by EXAFS (discussed later) indicates that the sample grown at 60 mTorr, having the lowest average roughness, most closely matches the ideal ferrite structure.

#### B. Magnetic properties

Figure 3(a) shows the variation of saturation magnetization as a function of substrate temperature. It is clear from this figure,  $4\pi M_s$  increases with substrate temperature approaching the bulk equilibrium value of 1700 G (Ref. 12) at 900 °C. In recent x-ray absorption studies we have found that at low pressures,  $\sim 1$  mTorr, there is incomplete oxidation of the ferrite film leading to a significant reduction in the saturation magnetization. In Fig. 3(b), the saturation magnetization is presented as a function of the oxygen pressure

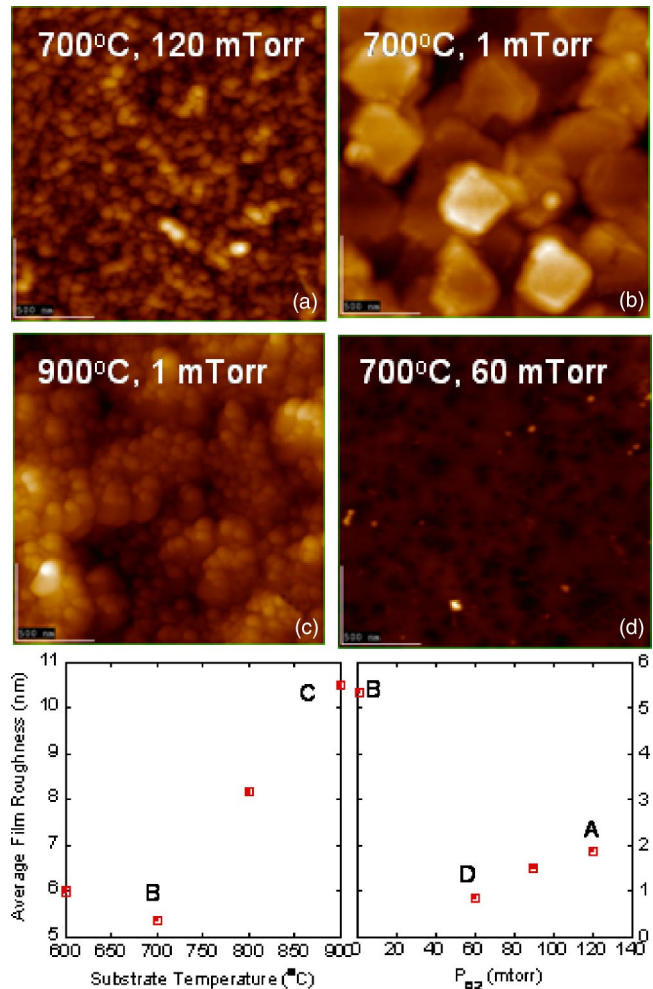


FIG. 2. Atomic force microscopy images for samples grown under various processing conditions (denoted on the figures). Average roughness values are plotted against substrate temperature and oxygen pressure used in PLD processing.

used in PLD processing. The magnetization increases with oxygen pressure reaching a maximum  $4\pi M_s$  of 2481 G at 90 mTorr. Pressures exceeding 90 mTorr lead to a reduction in magnetization. Compared with the bulk, this value represents a 42% increase in magnetization. Hysteresis loops of these films (not shown) reveal a strong uniaxial anisotropy. For the sample grown at 90 mTorr the coercive field was measured to be 163 Oe.

The samples prepared at 1 mTorr, 60 mTorr, 90 mTorr, and 120 mTorr were prepared for EXAFS analysis. The Fourier transform of the EXAFS data provides a real space radial structure function of the environment of the absorbing ion where the absolute amplitude of the function corresponds with the coordination and atomic order of atoms present at the radial distance. (Amplitude may also arise from multiple scattering events.) In these data the radial distance corresponds to bond distances that have been shifted in space by a unique electron phase shift. This phase shift must be calculated from (quasi) first principles and fit to the experimental data. The real part of the Fourier transform of the Cu and Fe EXAFS data for the 60 mTorr sample and the best fits are shown in Figs. 4(a) and 4(b), respectively. Values of the least square fitting parameter  $R$  range from 0.02–0.05. The fit re-

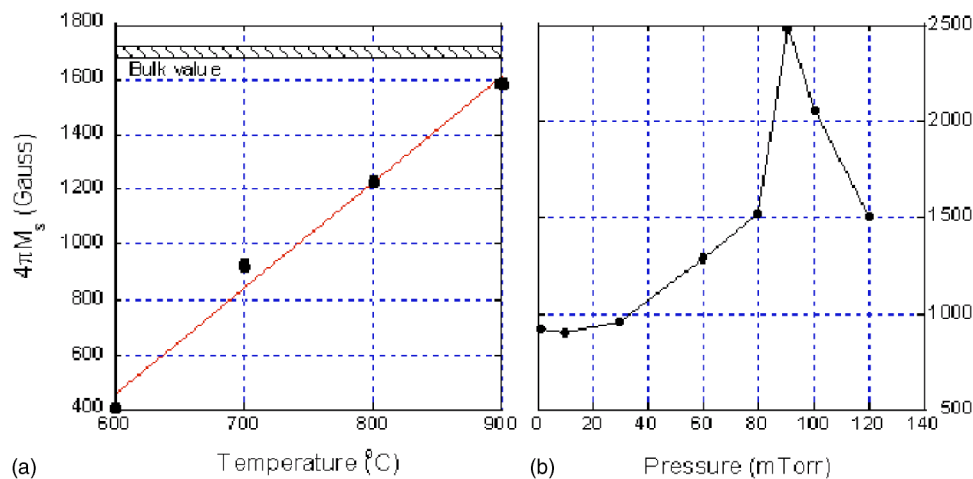


FIG. 3. Variation of saturation magnetization of copper ferrite films as a function of (a) substrate temperature and (b) oxygen pressure used in PLD processing.

sults allow for the determination of lattice parameters, oxygen displacement vector, and cation distribution. Other local atomic ordering parameters are also determined from this fitting procedure. From this analysis we measure the copper octahedral percentage changing from near its equilibrium value of 85% to  $\sim 50\%$  (at 90 mTorr). The fact that more copper cations reside on tetrahedral sites results in an increase in saturation magnetization. These findings agree with the theoretical prediction that an increase in the fraction of  $\text{Cu}^{2+}$  ( $\mu_B=1$ ) on the tetrahedral sublattice, and the corre-

sponding increase of  $\text{Fe}^{2+}$  ( $\mu_B=5$ ) on the octahedral sublattice, increases the net magnetization of the structure due to the magnetic imbalance between these sublattices.

## ACKNOWLEDGMENTS

This research was performed in part at the National Synchrotron Light Source at the Brookhaven National Laboratory which is sponsored by the Department of Energy. This research is also supported by the Office of Naval Research.

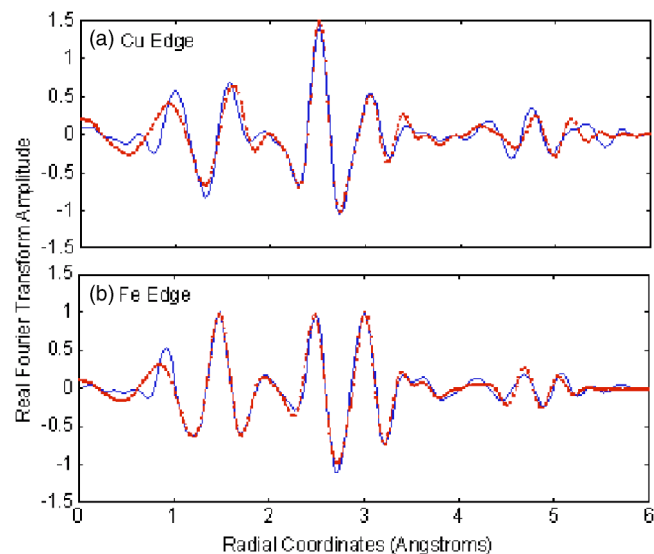


FIG. 4. Real Fourier transforms amplitude for (a) Cu and (b) Fe EXAFS data with best fits for the sample grown at 60 mTorr oxygen pressure and a substrate temperature of 700  $^{\circ}\text{C}$ .

<sup>1</sup>K.-H. Hellwege, Landolt-Bornstein, Numerical Data and Functional Relationships in Science and Technology (Springer-Verlag, Berlin, 1970), Vol. 4, Part b, p. 345.

<sup>2</sup>E. Prince and R. G. Treuting, Acta Crystallogr. **9**, 1025 (1956).

<sup>3</sup>M. Desai, S. Prasad, N. Venkataramani, I. Samajdar, A. K. Nigam, and R. Krishnan, J. Appl. Phys. **91**, 2220 (2002).

<sup>4</sup>R. A. Neiser, J. P. Kirkland, W. T. Elam, and S. Sampath, Nucl. Instrum. Methods Phys. Res. A **266**, 220 (1988).

<sup>5</sup>Data collection was performed using a total electron yield technique at beam line X23B at the National Synchrotron Light Source (Brookhaven National Laboratory, Upton, NY). At the time data were collected the storage ring energy was 2.54 GeV and the ring current ranged from 180–250 mA.

<sup>6</sup>V. G. Harris, N. C. Koon, C. M. Williams, Q. Zhang, M. Abe, and J. P. Kirkland, Appl. Phys. Lett. **68**, 2082 (1996).

<sup>7</sup>S. Calvin, E. E. Carpenter, V. G. Harris, and S. Morrison, Appl. Phys. Lett. **81**, 3828 (2002).

<sup>8</sup>J. J. Rehr, S. I. Zabinsky, and R. C. Albers, Phys. Rev. Lett. **81**, 3828 (2002).

<sup>9</sup>D. E. Sayers and B. A. Bunker, *X-Ray Absorption: Principles, Applications, Techniques of EXAFS, SEXAFS, and XANES* (Wiley, New York, 1988), Vol. 92, pp. 211–253.

<sup>10</sup>B. Ravel and M. Newville, Proceedings of the 12th Annual XAFS Conferences [Phys. Scr. (in press)].

<sup>11</sup>M. Newville, J. Synchrotron Radiat. **8**, 322 (2001).

<sup>12</sup>J. Smit and H. P. J. Wijn, *Ferrites* (Wiley, New York, 1959), p. 157.