

Cation engineering of Cu-ferrite films deposited by alternating target laser ablation deposition

Aria Yang,^{1,a)} Zhaohui Chen,¹ Shaheen M. Islam,² Carmine Vittoria,¹ and V. G. Harris¹

¹Center for Microwave Magnetic Materials and Integrated Circuits, Department of Electrical and Computer Engineering, Northeastern University, Boston, Massachusetts 02115, USA

²Department of Natural Sciences, Virginia Union University, Richmond, Virginia 23220, USA

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Epitaxial copper ferrite thin films were deposited on MgO substrates by the alternating target laser ablation deposition method. A series of films was studied to explore the impact of oxygen operating pressure, substrate temperature, and the ratio of laser shots incident on each target upon the magnetic, structural, and atomic structural properties. The highest saturation magnetization, 2800 G, was achieved at a 90 mTorr oxygen pressure and at 650 °C for the substrate temperature. This value is 65% higher than the room temperature magnetization for bulk equilibrium samples. The inversion parameter was measured by extended x-ray absorption fine structure analysis. The sample having the highest saturation magnetization had a corresponding inversion parameter (percentage of Cu ion octahedral site occupancy) of 51.5% compared with the bulk value of 85%. © 2008 American Institute of Physics. [DOI: 10.1063/1.2837646]

INTRODUCTION

Spinel ferrite has a closed packed oxygen lattice with transition metal cations residing at the interstices. In one unit cell of spinel ferrite, magnetic and often nonmagnetic ions incompletely occupy eight of the 64 tetrahedrally coordinated (*A*) sites and 16 of the 32 octahedrally coordinated (*B*) sites. The type, valence, and distribution of those transition metal cations determined the magnetic and electronic properties of the material. Copper ferrite in bulk form is typically a mixed spinel with approximately 85% of the Cu ions residing on the octahedral sublattice (inversion coefficient) with the remainder occupying the tetrahedral sites.¹ Density functional theory suggests that if a greater proportion of Cu²⁺ ions reside on the tetrahedral sublattice, the exchange constant will increase leading to an increase in the room temperature saturation magnetization.²

Earlier studies by Yang *et al.*³ employed conventional pulsed laser deposition (PLD) and showed that substantial increases in room temperature magnetization are indeed possible. Here, we used the alternating target laser ablation deposition (ATLAD) technique to explore the limits of cation-disorder-enhanced magnetization in the Cu-ferrite system. We have grown a series of copper ferrite films on (100) MgO substrates as a function of temperature, pressure, the growth rate, and the ratio of incident laser shots on each binary target. In order to obtain the structural information at the atomic level and the cation distribution, we applied the extended x-ray absorption fine structure analysis (EXAFS) technique. The EXAFS fitting procedures were outlined in the earlier studies.³ In this article, both Cu and Fe *K* edge EXAFS data were refined together using the codes of Athena and Artemis⁴ developed upon the IFEFFIT (Ref. 5) interactive program.

EXPERIMENTS

The CuFe₂O₄ films were grown using the KrF excimer laser at a wavelength of 248 nm ablating sequentially from two binary oxide targets of CuO and Fe₂O₃. We referred this technique as ATLAD and it has been used by us in the past to deposit ferrite films far from equilibrium. MgO substrates were selected because of its close lattice match [$a = 4.216 \text{ \AA}$ (Ref. 6)] with the Cu ferrite [$a = 8.445 \text{ \AA}$ (Ref. 7)]. The difference between the thermal expansion coefficients for MgO and CuFe₂O₄ is within 5%. In optimizing film growth conditions, we first deposited a series of films in which the substrate temperatures were varied from 550 to 750 °C with a fixed oxygen pressure of 90 mTorr. Following this study, we fixed the substrate temperature at the value determined best for maximum saturation magnetization (650 °C) and varied the oxygen pressures from 1 to 120 mTorr. The ratio of laser pulses on each of the CuO and Fe₂O₃ targets was fixed at 4:10 to maintain the stoichiometry of CuFe₂O₄. The laser energy was fixed at 250 mJ. The repetition rate was first fixed at 4 Hz and increased to a higher value while we studied the impact of growth rate. Similar growth conditions were applied during the conventional PLD growth (from a single CuFe₂O₄ target) for comparison purposes. The dc magnetic properties were measured at room temperature using vibrating sample magnetometry (VSM). For a quantitative characterization of short range order structure and cation distribution among those thin films, EXAFS technique was employed. Fe and Cu *K* edge absorption data were collected using fluorescence yield at beamline X23B at the National Synchrotron Light Source (NSLS) at room temperature. The storage ring energy was 2.8 GeV and the ring current ranged from 180 to 300 mA during the data collection.

RESULTS AND DISCUSSIONS

Cu *K*α x-ray diffraction θ - 2θ scans were performed to identify the phases in the films and to determine crystal tex-

^{a)}Electronic mail: fyang@coe.neu.edu.

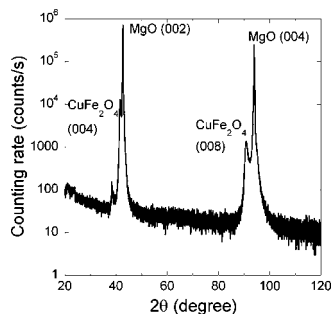


FIG. 1. Cu $K\alpha$ x-ray diffraction θ - 2θ scans of a CuFe_2O_4 film deposited on a (100) MgO substrate at an oxygen pressure of 30 mTorr.

ture properties. The results are plotted in Fig. 1 and show a film grown along the (100) substrate crystal direction with a strong crystal texture. Surface roughness for selected samples was examined by atomic force microscopy. The surface roughness of ATLAD grown samples showed an increase from 2.38 to 3.54 nm as the processing pressure increased from 60 to 120 mTorr, while the substrate temperature was maintained at 650 °C. The surface roughness is found to be relatively large compared to those processed under the same conditions by conventional PLD (0.863–1.88 nm). This might be due to the structural defects introduced by the layer-by-layer growth approach. The sample grown at a lower temperature (550 °C) and under the same processing pressure showed a larger surface roughness (10.4 nm).

The VSM measurement results were plotted in Fig. 2. The saturation magnetization is plotted as a function of both the substrate temperature and the oxygen pressure. The first set of experiments was carried out in pursuit of understanding the resulting film behavior under different substrate temperatures. The oxygen pressure was fixed at 90 mTorr, which was found to be the best growth condition in the earlier conventional PLD CuFe_2O_4 film study.³ From Fig. 2(a), we observed the magnetization increased to a maximum (1843 G) as the substrate temperature was increased to 650 °C. As we increased the substrate temperature to 700 °C, the magnetization drops sharply to 890 G and remained at the same level as we further increased the temperature to 750 °C. The repetition rate was fixed at 4 Hz during this study. The region between 600 and 650 °C results in the highest saturation magnetization values. These results can be understood from the standpoint of adatom mobility during film growth. The surface mobility of ions scales proportionally with the substrate temperature. At high temperatures, the Cu ions are more likely to find the lowest energy state or the distribution closest to equilibrium. In this case, that has Cu residing principally on the octahedral sublattice, thus resulting in a reduc-

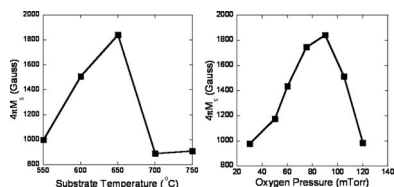


FIG. 2. The saturation magnetization was plotted as a function of (a) the substrate temperature and (b) oxygen pressure for the CuFe_2O_4 films.

tion of the J_{AB} exchange and a reduced saturation magnetization. The lower magnetization values in films grown at low temperatures are due to a residual amorphous component that is common in ferrite films grown below 550 °C.

We also investigated the effect of pressure on ATLAD Cu-ferrite films grown at a fixed temperature. We kept the substrate temperature at 650 °C and varied the chamber oxygen pressure from 1 to 120 mTorr. The background pressure was 10^{-6} Torr for all depositions. It is noticed that, with oxygen pressure lower than 30 mTorr, the ferrite films have low magnetic moments. This can be explained by the change in Cu valence from +2 to +1 due to oxygen deficiencies. Since Cu^{1+} ions have no Bohr magneton and the fact that Cu ions prefer B sites generally, the resulting copper ferrite thin films grown under low oxygen pressure may become antiferromagnetic. Here, we only report on the copper ferrite ATLAD films grown above 30 mTorr since these have attractive magnetic properties. The saturation magnetization of copper ferrite films is shown as a function of oxygen pressure in Fig. 2(b). It is seen that the magnetization slowly increased as we increased the oxygen pressure from 30 to 75 mTorr, and reached its highest value at 650 °C and 90 mTorr. The shape of the magnetization versus oxygen pressure curve is similar to that obtained from the conventional copper ferrite study.⁸ The trends in magnetization with oxygen pressures above 30 mTorr can be understood from the standpoint of ion-plasma interaction. For example, as the pressure is increased, the ablated ions increasingly experience collisions within the plasma reducing their kinetic energy and subsequently their surface mobility. This leads to a greater randomization of cation distribution with the lattice and higher magnetization. For samples grown at the highest pressure, the plasma interacts with the growing film and increases the adatom mobility, thus reducing the disorder. This model of PLD film growth was first put forward by Yang *et al.* in Ref. 3.

Based upon the observations, we conclude that to achieve the highest magnetization, the copper ferrite films should be deposited at temperatures around 650–700 °C and at an oxygen pressure of 75–90 mTorr. However, although the highest magnetization was observed at 650 °C and at 90 mTorr oxygen pressure, we noticed that the magnetization value is not as high as what we have measured previously. It is known that the PLD technique has the advantage of maintaining the stoichiometry of the target material. However, by ATLAD, the growth rate for CuO and Fe_2O_3 may not be the same under the same growth conditions. Therefore, we fine tuned the ATLAD process to produce copper ferrite to achieve lower cation inversion and higher magnetization.

During the course of the previous depositions, we noticed that the deposited film thickness cannot be less than 0.1 μm to maintain a reasonable magnetization (>1000 G). On the other hand, prolong deposition time may lead to the diffusion of MgO. As a result, we increased the growth rate by increasing the repetition rate from 4 to 12 Hz. At the same time, preserving the same ratio of laser shots incident upon each target, the number of shots were doubled for both targets. With all these changes, the resulting deposition time for each sample was still about 4 h. With consideration of the

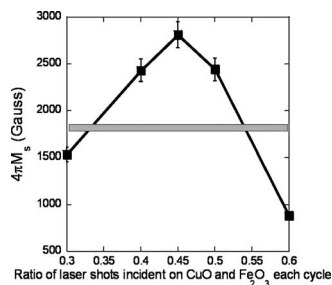


FIG. 3. The saturation magnetization was plotted as a function of the ratio of laser shots incident on two binary (CuO and Fe₂O₃) targets, at an increased growth rate for the CuFe₂O₄ films.

different growth rates for each target, we varied the ratio of laser shots on CuO and Fe₂O₃ targets from 0.3 to 0.6. The results are shown in Fig. 3.

Since we started the ATLAD experiments using a target shot ratio of 0.4, we did not go beyond the 0.6 ratio as we found the magnetization already dropped to a very low level. There is no reason to increase the ratio beyond 0.6 since that would increase the Cu content in the film and reduce the net magnetic moment since the Bohr magneton of Cu²⁺ ($1\mu_B$) is far less than that of Fe³⁺ ($5\mu_B$). It is noteworthy that as we increased the growth rate, the magnetization increased to 2433 G at a ratio of 0.4 at 90 mTorr, which is 43% higher than the bulk value. Furthermore, the saturation magnetization reached 2813 G (65% higher) at a ratio of 0.45.

EXAFS data of a series of samples prepared at different oxygen pressures and the sample with the highest saturation magnetization were collected using beamline X23B at the NSLS. The Fourier transform (FT) of the EXAFS data provides a real space radial structure function of the environment of the absorbing ion. The absolute amplitude of the function corresponds with the coordination and atomic order of atoms present at the radial distance. The real part of the FT of the Fe and Cu *K* edges EXAFS data for the 90 mTorr, 650 °C 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 to 0.05. The fit results allow one for the determination of lattice parameters, oxygen displacement vectors (*u*), cation distribution, and other local atomic ordering parameters. The saturation magnetization of the samples

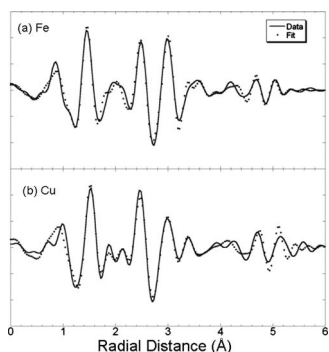


FIG. 4. EXAFS data as the real part of the Fourier transform from (a) Fe and (b) Cu *K*-edge absorptions (solid curve) with best fit data (dot) for a CuFe₂O₄ film deposited on a (100) MgO substrate at an oxygen pressure of 90 mTorr 650 °C.

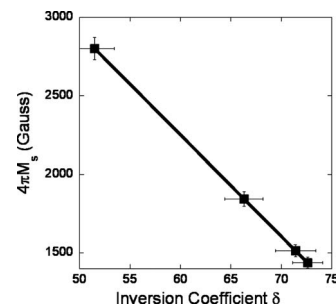


FIG. 5. The saturation magnetization was plotted as a function of inversion parameter (i.e., the percentage of Cu residing at *B* sites).

was plotted in Fig. 5 as a function of inversion parameter, i.e., the percentage of Cu ions residing at *B* sites. These data are clearly in agreement with the previous findings of PLD Cu-ferrite films.³ Higher magnetization corresponds to a lower inversion parameter. Whereas for the sample with the highest magnetization, we measured a decreased of 51.5% cation inversion compared with 85% of the bulk value. By ATLAD growth technique, we indeed modified the cation distribution of the Cu-ferrite films and further increased the magnetization by fine tuning the growth rate and the stoichiometry. The ATLAD growth technique provides a new approach to the design of novel microwave ferrites for nonreciprocal devices.

CONCLUSIONS

By ATLAD growth, we have grown several series of CuFe₂O₄ thin films on (100) MgO substrates. It was found that those conditions leading to high growth rates resulted in a lower cation inversion (i.e., a greater fraction of Cu ions on the tetrahedral sublattice) and subsequently higher magnetization values. The highest saturation magnetization value (2813 G) was measured from the sample deposited at 90 mTorr and 650 °C. This represents a 65.5% increase in room temperature saturation magnetization above that of the equilibrium value of 1700 G. By using extended x-ray absorption fine structure measurements and modeling, we determined that the inversion parameter of CuFe₂O₄ was 51.5% compared to the equilibrium value of 85%.

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