

## Fabrication of Magnetoresistive Thin Films Having GMR/CMR Effect as Magnetic Sensors Using Pulsed Laser Ablation Technique

Abdul Halim Shaari, Elias Salon, Chow Sai Pew, Hishamuddin Zainuddin

Faculty of Science and Environmental Studies  
Universiti Putra Malaysia  
43400 UPM, Serdang, Selangor  
Malaysia

Telephone Number of Corresponding Author: 03-89466648

E-mail of Corresponding Author: ahalim@fsas.upm.edu.my

**Key words:** Colossal Magnetoresistance, Giant Magnetoresistance, Manganite, Pulsed Laser Ablation Deposition, Magnetic Sensor

### Introduction

Magnetic thin films based on the giant magnetoresistance (GMR) and colossal magnetoresistance (CMR) effects are currently being used as sensor head in the magnetic data storage technology. With the technological revolution in the magnetic recording world of last decades, a need for better and more sensitive magnetoresistance materials as head sensing elements arises. GMR effect is commonly observed in magnetic multilayers films (Zhang and Levy 1991). However this effect is now observed in granular films, which composed of magnetic entities embedded in metallic matrix (Andres et al 1999). The larger the magnitude of the MR, for the relevant magnetic field strength, the more useful is the material. This can be accomplished by modifying the alloying compositions of the films. The effect is a useful property for detecting magnetic fields and is used to read the state of magnetic bits in advanced magnetic disk drives. Dramatic changes in resistance upon application of a magnetic field are also observed in manganese perovskite R-A-Mn-O ceramics (R-rare earth elements; A- divalent alkaline earth ion). This material that has a much higher MR values called CMR materials is also being research into. Early studies on the structure, magnetic and transport properties of R-Mn-O<sub>3</sub> (R-La, Pr) showed that this material is insulating. However by doping with some divalent alkaline element, the perovskite show interesting magnetic behaviour and transport properties. These impurities function as acceptors transforming the initially antiferromagnetic and insulating crystals into ferromagnetic and highly conductive materials.

### Materials and Methods

This research work involved in the synthesis of bulk Colossal Magnetoresistance (CMR) materials of La-Ca-Mn-O (LCMO) and La-Sr-Mn-O (LSMO) and La-Ba-Mn-O (LBMO) systems synthesized using conventional mixed-oxide solid state sintering method and coprecipitation method. The effect of doping of various elements on Ca, La or Mn sites was also studied. The bulk properties of the ceramics were carried out. Pulsed Laser Ablation Deposition (PLAD) system, developed at UPM, was used to deposit thin films were on glass substrates at substrate temperature less than 400°C. Besides CMR films, Giant Magnetoresistance (GMR) films had also been fabricated using Pulsed Laser Deposition and RF Magnetron Sputtering system. The films are based on the alloys of magnetic elements being embedded in the non-magnetic matrix's, such as Co-Ag, Ni-Fe-Cu. The films are termed as granular films. Surface and crystalline of the films were studied using SEM, AFM and XRD. The MR values were measured using a four-point probe technique. The electrical resistance was measured in the temperature range of 20-300 K by a standard four-point technique using a constant current source of 24 mA. Ac susceptibility measurements were performed in then temperature range of 20-300K using an Ac suseptometer (Lake shore Cryotronics- Model 7000). Identification of phases was done using a Siemens XRD machine with Cu K $\alpha$  radiation. SEM observed the microstructure of the samples. MR was measured between 77 K to room temperature in the applied dc field of 0-1 Tesla, using a spring-loaded four-point probe.

### Results and Discussion

The electrical resistance of the LCMO and LBMO materials in zero applied fields showed a semiconductor-metal transition at temperatures lower than room temperature. This transition may be Anderson-Mott transition, as discussed by Beltiz and Kirkpatrick. At about the same temperature, this material also exhibits ferromagnetic-paramagnetic transition. This phenomenon is explained using the double exchanged mechanism. Phase transition was also studied by doping LCMO and LBMO with either magnetic or non-magnetic elements. Magnetic elements tend to destroy the ferromagnetism more than the non-magnetic elements (Koh 2001). Bulk CMR materials show exciting magnetic and transport behaviour, where at a particular temperature, this material exhibits Anderson-Mott transition as well as ferromagnetic-paramagnetic transition. These phenomena could be explained via double exchange mechanism.

Thin films of the manganite or magnetic alloys fabricated via pulsed laser ablation method or RF sputtering shows the following characteristics;

- i) The temperature dependence of the resistance of bulk and film samples show metal-like behaviour, observed for the entire range of measurement (50K to 300K) for the LSMO bulk sample. From previous report,  $T_p$  for LSMO bulk is about 330K. Hence, metal-insulator transition ( $T_p$ ) is not observed here. In this region, the electrical transport mechanism that is dominant is the double exchange (DE) mechanism, which bring along the ferromagnetism. However,  $T_p$  for both 3.5  $\mu\text{m}$  and 1.7  $\mu\text{m}$

films drop at around 175K. This could be related to the presence of superparamagnetism (SPM) or grain boundaries (GBs) region where DE mechanism is discontinued or blocked and hence lowering the electrical transportation.

ii) The as-deposited ceramic film shows amorphous phase and will transform to polycrystalline state when heat treatment is applied. The magnetic property of the film is only moderately changed, while the resistivity and magnetoresistance are strongly affected. The trend of CMR curve for the ceramic film is quite similar in higher temperature. But at low temperature, it shows higher CMR value due to the polarization of electrons in the magnetically disordered regions near the grain boundaries.

iii) Low field effect of CMR was observed in the LSMO system.

iv) The GMR effect is highly influenced by the shape, size and distribution of the magnetic entities, which can be controlled by preparation condition and post annealing, and also composition and thickness of the films. The highest GMR value for  $\text{Ag}_{87.0}\text{Fe}_{9.5}\text{Co}_{3.5}$  granular film is about 7.6% measured at room temperature.

### Conclusions

The following conclusions can be made;

i) The low field effect of CMR films in the LSMO system at room temperature is a potential candidate as sensor elements for magnetic device applications.

### Benefits from the study

This study provides the following informations;

i) Colossal magnetoresistive thin films can be successfully fabricated by pulsed laser ablation method and RF sputtering.

ii) The films with huge MR are good candidate for potential applications as magnetic sensor elements that can be incorporated into MEMS technology.

iii) Magnetic films in the form of multilayers and spinvalve can be fabricated using these techniques.

iv) The technical know-how on the aspect of Pulsed Laser Ablation can be rendered to other potential users.

### Patent(s), if applicable:

Nil

### Stage of Commercialization, if applicable:

Nil

### Project Publications in Refereed Journals

- 1 Huda Abdullah, Halim SA, Lim Kean Pah, Kabashi Khatir Kabashi, Yu Ong Seng, Wan Mahmood Mat Yunus and Elias Saion, 2002 "Studies of Giant Magnetoresistance of Sputtered  $\text{Co}_{23.32}\text{Ag}_{76.68}$  Granular Magnetic Thin Film" *J. Solid St. Sci. Technol Letts.*, Vol. 9, no. 1, 74-80
- 2 Kabashi KK, Halim SA, Lim KP, Huda A, Abdullah Chik, Yu SO, Koh SF, Zainuddin H and Talib ZA, 2002 "Magnetoresistance Effect in  $\text{CoNiAg}$  Granular Thin Films Formed By Rf Sputtering System" *J. Solid St. Sci. Technol Letts.*, Vol. 9, no. 1, 221-225
- 3 Lim KP, Halim SA, Kabashi KK, Yu OS, Huda A, Zainuddin H and Chow SP. 2002 "Giant Magnetoresistance and Structural Studies of  $\text{Ag}_{82.2}\text{Fe}_{9.9}\text{Co}_{7.9}$  Granular Films" *J. Solid St. Sci. Technol Letts.*, Vol. 9, no. 1, 233-237
- 4 Lim KP, Halim SA, Kabashi KK, Yu OS, Koh SF, Huda A, Zainuddin H and Chow SP, 2001 "GMR of  $\text{Ag-Co-Fe}$  Granular Films" *J. Solid State Science and Technol. Letts*, Vol 8, No. 1&2 p89-93.

### Project Publications in Conference Proceedings

- 1 K.P.Lim, S.A.Halim, S.P.Chow and H. Zainuddin, "Microstructure Studies of Manganites Oxide Ceramics", Proc., Update on Microscopy and Microanalysis, (2002), p55-56
- 2 Abdullah Chik, S.A.Halim, K.P.Lim, Imad Hamadneh, Z. Gebrel and M. N. Dalimin "Structural, Magnetic and Electrical Properties of  $(\text{La}_{1-x}\text{In}_x)_{2/3}\text{Ca}_{1/3}\text{MnO}_3$ " Proc., Seminar Kebangsaan Sains, Teknologi dan Sains Sosial (2002), Jilid 2, p291-297.
- 3 K.K.Kabashi, S.A.Halim, K.P.Lim, A.Huda, H. Zainuddin, Z.A.Talib, and W.M.Y.W. Daud: "Influence of annealing time on MR effect of  $\text{CoNiCu}$  granular thin films", Proc. 2002 Postgraduate Seminar (2002), p50-55.
- 4 Z. Gebrel, S.A.Halim, Abdullah Chik, Imad Hamadneh, K.P.Lim and W. M. Daud W. Yusoff "Electrical and Magnetic Properties of Sm doped  $\text{La-Ca-MnO}_3$ " Proc., Seminar Kebangsaan Sains, Teknologi dan Sains Sosial (2002), Jilid 2, p310-313.
- 5 Z.Gebrel and S.A.Halim: "Electrical and magnetic properties of Sm doped LCMO", Proc. 2002 Postgraduate Seminar (2002), p115-120.
- 6 M.S.Sharmawati, S.A.Halim, M.Y.W.Mahmood and Z.Hishamuddin: "Electrical conductivity in Dy doped LCMO perovskite", Proc. 2002 Postgraduate Seminar (2002), p144-147.

- 7 K.P.Lim, S.A.Halim, H. Zainuddin, S.P.Chow and W.M.Y.W. Daud: "Surface morphology and electrical Studies of Manganites Oxide Film", Proc. 2002 Postgraduate Seminar (2002), p1-5.
- 8 S.A. Halim, K.P.Lim, S.P. Chow, H. Zainuddin, S.F.Koh and Abdullah Chik "Effect of vanadium doping on the Semiconducting properties of  $La_{0.67}Ca_{0.33}MnO_3$  Ceramics" Proceedings ICSE 2002: IEEE International Conference on Semiconductor Electronics (2002) p534-538.
- 9 K.P.Lim, S.A.Halim, K.K.Kabashi, O.S.Yu, A. Huda, H. Zainuddin and S.P.Chow "Giant Magnetoresistance and Structural Studies of  $Ag_{82.2}Fe_{9.9}Co_{7.9}$  Granular Films" *J. Solid St. Sci. Technol Letts.*, Vol. 9, no. 1, 233-237(2002)
- 10 S.A. Halim, K.P.Lim, S.P. Chow, H. Zainuddin, S.F.Koh and Abdullah Chik "Effect of vanadium doping on the Semiconducting properties of  $La_{0.67}Ca_{0.33}MnO_3$  Ceramics" Proceedings ICSE 2002: IEEE International Conference on Semiconductor Electronics (2002) p534-538.
- 11 K. K.Kabashi, S. A. Halim, K. P. Lim, Abdullah Chik, Huda Abdullah, M. S. Sharmiwati, H. Zainuddin and Z.A.Talib "Giant Magnetoresistance of  $AgCoFe$  Thin Films For Magnetic Field Sensors" AsiaSENCE 2003 Sensor, 59-64(2003).
- 12 Abdullah Chik, S. A. Halim, M. S. Sharmiwati, K. P. Lim, Z.Gebrel, K. K.Kabashi, M.M.Dihom, W.M.M. Yunus, M.M. Mokhsin and M.N. Dalimin "Electrical and Magnetic properties of Ga Substituted  $La_{2/3}Ca_{1/3}MnO_3$  Perovskite" AsiaSENCE 2003 Sensor, 73-77(2003).
- 13 K. P. Lim, S. A. Halim, H. Zainuddin, S.P.Chow, Abdullah Chik, M. S. Sharmiwati, and H.A.A.Sidek "Colossal Magnetoresistance of  $La-Ca-Mn-O$  Thin Films" AsiaSENCE 2003 Sensor, 69-72(2003).
- 14 Hazar A. Salama, S.A. Halim, Noorhana Yahya, Zaidan Abdul Wahab, Imad Hamadneh and Z. Gebrel," Structure and Electrical Properties of  $La_{2/3}Ca_{1/3}MnO_3$  Perovskites" Proceedings, 5<sup>th</sup> Putra Physics Seminar 2003, 77-80(2003).
- 15 R.E. Shaiboub, S.A. Halim, Y.B. Noorhana, A.W. Zaidan and K.P. Lim ," Effect of Sn doping in  $La_{2/3}Sr_{1/3}Mn_{1-x}Sn_xO_3$  ( $x \leq 0.15$ ) " Proceedings, 5<sup>th</sup> Putra Physics Seminar 2003, 209-213(2003).
- 16 Z. Gebrel, S.A. Halim, Hishammuddin Zainuddin, Z.A. Talib, Abdullah Chik and Hazar A. S," Colossal Magnetoresistance Properties of  $(La_{1-x}Er_x)_{0.67}Ca_{0.33}MnO_3$ " Proceedings, 5<sup>th</sup> Putra Physics Seminar 2003, 308-313(2003).
- 17 K.K.Kabashi, S.A.Halim, K.P.Lim, O.S.Yu, S.F.Koh, A.Huda, H.Zainuddin and Z.A.Talib, "The effect of Composition and Thermal treatment on the Magnetoresistance of  $CoNiAg$  Granular Thin Films," Proc., Malaysian Science and Technology Congress, (2001), p97-102.
- 18 K.P.Lim, S.A.Halim, K.K.Kabashi, O.S.Yu, A. Huda, S.P.Chow and H. Zainuddin, "The Giant Magnetoresistance Studies of  $Ag_{87.5}Fe_{9.5}Co_{3.5}$  Granular Films", Proc., Malaysian Science and Technology Congress, (2001), p517-524.
- 19 S.F.Koh, S.A. Halim, S.P. Chow, H.Zainuddin. K.P.Lim, O.S.Yu and K.K.Kabashi "Effect of Zirconium doping on the Magnetic and Electronic Properties  $La_{0.67}Ca_{0.33}Mn_{1-x}Zr_xO_3$  Ceramics" Proceedings of the Postgraduate Seminar, UPM 2000, p90-97, (2000)
- 20 S.F.Koh, S.A. Halim, K.P.Lim, K.K.Kabashi, O.S.Yu, W.D.W.Yusoff, S.P.Chow, H. Zainuddin and S.B.Mohamed "Low temperature Colossal Magnetoresistance of  $La-Ca-Mn-O$  Ceramics" Solid State Science and Technology, 8(1&2) (2000) 61-66.
- 21 K.P.Lim, S.A. Halim, K.K.Kabashi, O.S.Yu, S.F.Koh, W.M.Yunus and S.P.Chow "GMR of Sputtered  $Ag_{60.3}Ni_{17.3}Fe_{22.4}$  Granular Magnetic Thin Films" Solid State Science and Technology, 8(1&2) (2000) 74-79.
- 22 K.K.Kabashi, S.A. Halim, K.P.Lim, S.F.Koh, O.S.Yu, S.P.Chow and H.Zainuddin "GMR in granular  $Co-Ag-Cu$  thin films prepared by RF magnetron deposition" Solid State Science and Technology, 8(1&2) (2000) 114-119.
- 23 S.F.Koh, S.A. Halim, K.P.Lim, K.K.Kabashi, O.S.Yu, S.P.Chow and H. Zainuddin "Colossal Magnetoresistance of Vanadium Doped  $La-Ca-Mn-O$  Ceramics" Proceedings International Conference on Advances in Strategic Technologies, ICAST 2000, Vol 1, p 567-575 (2000)
- 24 Yu, O.S., Halim, S.A., Lim, K.P., Kabashi, K.K.and Koh, S.F. "Thickness and Temperature Dependences of GMR in  $CoCu$  and  $CuCoNi$  Granular Films" Proceedings International Conference on Advances in Strategic Technologies, ICAST 2000, Vol 1, p 621-626 (2000)
- 25 S.A. Halim, S.F.Koh, S.P.Chow, H.Zainuddin, K.P.Lim, O.S.Yu, and K.K.Kabashi "Effect of Zr Doping on The Semiconducting Properties of  $LaCa MnO$  Ceramics" Proceedings International Conference on Semiconductor Electronics, ICSE 2000, p 255-260 (2000)
- 26 O.S.Yu, S.A. Halim, K.P.Lim, K.K.Kabashi, S.P.Chow, H. Zainuddin, and S.F.Koh, "Influence of Annealing Temperature On Magnetoresistance of Cobalt-Copper Granular Films" Proceedings PERFIK 2000, p509-515, (2000)
- 27 S.F.Koh, S.A. Halim, K.P.Lim, K.K.Kabashi, O.S.Yu, S.P. Chow, H.Zainuddin, and W.D.W.Yusof "Colossal Magnetoresistance of Low Zirconium Doped  $LaCaMnO$  Ceramics" Proceedings PERFIK 2000, p501-508, (2000)
- 28 K.P.Lim, S.A. Halim, S.P.Chow, H. Zainuddin, K.K.Kabashi, O.S.Yu and S.F.Koh, "Temperature and Thickness Dependences of GMR of Silver-Iron Granular Films" Proceedings PERFIK 2000, p437-444, (2000)
- 29 O.S. Yu, S.A. Halim, K.P. Lim, K.K. Kabashi, A.Huda, H. Zainuddin and SP.Chow "Magnetoresistance effect in  $AlFeNi$  granular thin film" Proc. NSM 2001., IEEE National Symposium on Microelectronics, p287-291

30 S.A.Halim, S.F. Koh, K.P. Lim, H. Imad and H.A.A. Sidek, "Colossal Magnetoresistance of Zirconium doped Manganite Perovskite"  
Presented at International Conference on Materials for Advanced Technologies (ICMAT 2001), Singapore, Abstract p118.

*Graduate Research*

	Name of Graduate	Research Topic	Field of Expertise	Degree Awarded	Graduation Year
1.	Lim Kean Pah(Malaysia);	Studies of GMR and CMR Thin films Using Laser Ablation Deposition Technique	Magnetoresistive materials	PhD	2002
2.	Yu Ong Seng(Malaysia)	Magnetoresistance of CoCuNi, CuCo and AlNiFe Granular Thin Films Prepared by Rf Sputtering	Magnetoresistive materials	MSc	2002
3.	Huda Abdullah(Malaysia)	Studies of Tertiary GMR films by Magnetron Sputtering	Magnetoresistive materials	MSc	2002
4.	Zohra Ali Gabriel(Libya)	Colossal Magnetoresistance of $(La_{1-x}A_x)_{0.67}Ca_{0.33}MnO_3$ (A = Sn, Sm, Er) Perovskite	Magnetoresistive materials	MSc	2003
5.	Sharmiwati Mohamad Sharif (Malaysia)	Microstructural, Electrical and Magnetic Properties of $(La_{1-x}Dy_x)_{1-y}Ca_yMnO_3$ ( $x=1/8, 1/3, 1/2$ ); ( $y=0.0-1.0$ ) Perovskite	Magnetoresistive materials	MSc	2003

IRPA Project number: 09-02-04-0148  
UPM Research Cluster: MEE