ELECTRICAL AND MAGNETORESISTIVE PROPERTIES OF Ag-Co/Cu-Fe THIN FILMS AND BULK RARE-EARTH MANGANESE PEROVSKITE (Ln-Ba-Mn-O)

By

HUDA ABDULLAH

Thesis Submitted to the School of Graduate Studies, Universiti Putra Malaysia, in Fulfilment of the Requirements for the Degree of Doctor of Philosophy

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DEDICATION

Special dedication to:

In memory of my beloved father,
Hj. Abdullah Abd. Rahman (who left this world on
20th August 2004)
May Allah bless him, Amin…

My beloved mother, Hajjah Raihal Lamshiah,
my brothers, younger sister and sisters in-law
- *for love and caring…*

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This dissertation presents the study of granular thin films of Ag-Co-Fe and Ag-Cu-Fe alloys prepared by Radio Frequency (RF) Magnetron Sputtering Technique and doped with Pr, Nd, Al, Ru and Pd on Ln-Ba-Mn-O perovskite manganates (Ln=rare-earth). The main objective is to the electrical resistance and magnetoresistance of the Ag-Co-Fe and Ag-Cu-Fe thin film and rare earth perovskite system. In order to achieve this objective, several characterizations needed to be performed, such as Scanning electron microscopy (SEM), Energy dispersive X-ray (EDX) analysis, atomic force microscope (AFM), X-Ray diffraction (XRD) measurement, magnetoresistance (MR) measurement and resistivity measurement. The surface morphology of thin film examined using a SEM and AFM, was found to be smooth and homogeneous. The elemental composition was determined through EDX. The optimum content of the magnetic element was about 10%,

20%, 5% and 13% for AgCo2Fe2, AgCo2Fe3, AgCu2Fe2 and AgCu2Fe4 alloys, respectively. The crystal structure of the materials were analysed using a PHILIPS X-ray diffractometer. XRD diffractogram for the as-deposited films consists of (111), (200), (220) and (311) textured structure of Ag, which is dominated by (111) peak. The magnetoresistance (MR) effect was measured using a standard four-point probe technique and the measurements were performed at the room temperature and also at lower temperatures down 90 K. The lower temperatures were achieved using liquid nitrogen cryostat. Overall, MR increased with the decrease in temperature of the samples. The maximum MR value of 3.17%, 2.85% and 2.65% at 1 Tesla were obtained for the series of AgCo2Fe2 (T_s=300^{o}C), AgCu2Fe2 (T_s=300^{o}C) and AgCu2Fe4 (T_s=250^{o}C), respectively which were measured at 90K. At the room temperature, the MR values for the AgCo2Fe2 and AgCu2Fe4 were higher than that of MR of AgCo2Fe3 and AgCu2Fe2 samples. The highest MR value at 1 Tesla for the annealed sample of AgCo2Fe2 (T_s=150^{o}C) which was deposited for 120 minutes was about 3%, when the sample was annealed at 400^{o}C for 60 minutes. The structural, electrical and magnetic properties of colossal magnetoresistance $La_{2/3}Ba_{1/3}MnO_3$ and $La_{1/2}Ba_{1/2}MnO_3$ doped with Pr, Nd, Al, Ru and Pd, while $Pr_{2/3}Ba_{1/3}MnO_3$ was doped with Nd were also studied. Samples with various concentration of the dopant were prepared using solid state reaction method. XRD diffractogram showed a single phase pattern at low concentration with higher intensity of secondary phase at high concentration of the dopant. All samples showed the distorted orthorhombic structure. The electrical properties showed that the samples exhibited metal to insulator transition (MIT) characteristics except samples doped with Pd and Ru. Beyond specific doping level, the samples become insulator for Mn-site

substitution and semiconducting behaviour for La-site substitution. This phenomenon occurred due to the smaller ionic size of dopant for La and Mn site substitution. Zener double exchange polynomial $\rho = \rho_0 + \rho_2 T^2 + \rho_n T^n$, was observed well below the metal-insulator transition (T_p) temperature. Variable Range Hopping model and Adiabatic Small Polaron Hopping model well fitted at high temperature regime and values of the activation energy (E_a), density of states $N(E_F)$, Debye temperature (θ_D) and phonon frequency (v) could be estimated. It showed that E_a for all samples were within the range of ~30 meV to ~180 meV. Magnetoresistance measurement showed that MR ratio increased when decrease in temperature and and increase in dopant concentration. The maximum values of MR at La-site substitution was higher than at Ba-site and Mn-site substitutions. The highest MR value was 63.491% for sample $(La_{1-x}Nd_x)_{1/2}Ba_{1/2}MnO_3$ (x=1) measured for 150 K at 1 Tesla. All samples exhibit low-field magnetoresistance (LFMR) and high-field magnetoresistance (HFMR) regions except $(La_{1-x}Nd_x)_{1/2}Ba_{1/2}MnO_3$ samples. The LFMR ratio reduced with increasing temperature. The SEM micrographs indicated the grains sizes were reduced and level of porosity increased as the dopant content increased which can be seen in all samples except $La_{2/3}(Ba_{1-x}Pd_x)_{1/3}MnO_3$.

Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia sebagai memenuhi keperluan untuk ijazah Doktor Falsafah

PENCIRIAN ELEKTRIK DAN MAGNETORINTANGAN FILEM NIPIS Ag-Co/Cu-Fe DAN BAHAN PUKAL PEROVSKIT NADIR BUMI (Ln-Ba-Mn-O)

Oleh

HUDA BINTI ABDULLAH

Mei 2006

Pengerusi: Profesor Abdul Halim Shaari, PhD

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Dessertasi ini mempersembahkan kajian mengenai filem nipis berbutir daripada aloi Ag-Co-Fe dan Ag-Cu-Fe yang disebabkan menggunakan Teknik Percikan Frekuensi radio Magnetron dan pendopan Pr, Nd, Al, Ru dan Pd pada manganat perovskit $Ln_{1-x}Ba_xMnO_3$. Objektif utama kajian ini adalah untuk mengkaji kerintangan elektrik dan magnetorintangan filem nipis Ag-Co-Fe dan Ag-Cu-Fe dan sistem perovskit nadirbumi dilakukan. Untuk mencapai objektif ini, beberapa pencirian perlu dilakukan menggunakan mikroskop imbasan elektron (SEM), analisis sinar-x sebaran tenaga (EDX), mikroskopi daya atom (AFM), belauan Sinar-X (XRD), pengukuran magnetorintangan (MR) dan pengukuran rintangan elektrik. Morfologi permukaan bagi filem-filem nipis telah diperiksa menggunakan SEM dan AFM, dan didapati morfologi permukaan adalah licin dan homogen. Komposisi unsur-unsur untuk setiap siri telah

ditentukan menggunakan analisis sinar-X sebaran tenaga (EDX). Peratusan optimum bahan magnet dalam sampel AgCo2Fe2, AgCo2Fe3, AgCu2Fe2 dan AgCu2Fe4 masing-masing adalah kira-kira 10%, 20%, 5% and 13%. Struktur hablur bahan dianalisis dengan menggunakan Pembelau Sinar-X (XRD) PHILIPS. Spektra XRD menunjukkan set puncak-puncak (111), (200), (220) dan (311) telah diperhatikan. Puncak (111) Ag menunjukkan keamatan yang tinggi dan dominan. Puncak (111) Ag melebar, maka nilai MR akan meningkat. Kesan magnetorintangan diukur menggunakan teknik kuar empat titik piawai dan pengukuran dilakukan pada suhu bilik dan suhu lebih rendah hingga 90K. Suhu rendah dicapai dengan menggunakan kriostat nitrogen cair. Secara keseluruhan, nilai MR meningkat dengan penurunan suhu sampel. Nilai maksimum MR iaitu 3.17%, 2.85% dan 2.65% pada 1 Tesla masing-masing diperolehi bagi filem nipis AgCo2Fe2 (suhu pengenapan, T_s=300^{o}C), AgCu2Fe2 (T_s=300^{o}C) dan AgCu2Fe4 (T_s=250^{o}C) yang diukur pada 90 K. Pada suhu bilik, nilai MR untuk sampel AgCo2Fe2 dan AgCu2Fe4 lebih tinggi berbanding dengan sampel AgCo2Fe3 dan AgCu2Fe2. Nilai tertinggi MR pada 1 Tesla bagi sampel AgCo2Fe2 (suhu pengendapan 150^{o}C) yang disepuh lindap pada 400^{o}C selama 60 minit ialah lebih kurang 3%. Kajian-kajian pencirian struktur hablur, sifat elektrikal dan magnet telah dijalankan bagi bahan-bahan Pr, Nd, Al, Ru dan Pd digantikan pada sebatian $La_{2/3}Ba_{1/3}MnO_3$ dan $La_{1/2}Ba_{1/2}MnO_3$, sementara Nd digantikan pada $Pr_{2/3}Ba_{1/3}MnO_3$. Sampel-sampel yang mengandungi pelbagai kandungan bahan pendopan telah disediakan dengan kaedah tindakbalas keadaan pepejal. Corak belauan sinar-X menunjukkan fasa tunggal pada kepekatan rendah dengan penambahan keamatan fasa kedua pada kepekatan pendopan yang tinggi. Semua sampel menunjukkan struktur ortorombik herot. Daripada sifat elektrik menunjukkan sampel-sampel

mempamerkan sifat peralihan logam kepada penebat kecuali sampel-sampel yang didopkan dengan Pd dan Ru. Selepas mencapai sesuatu paras pendopan tertentu, sampel-sampel menjadi penebat bagi penggantian di bahagian Mn dan bersifat semikonduktor bagi penggantian di tapak La. Fenomena ini disebabkan oleh saiz ionic pendopan mengecil bagi penggantian di tapak La dan Mn. Polinomial pertukaran ganda dua Zener, $\rho = \rho_0 + \rho_2 T^2 + \rho_n T^n$ diperhatikan pada suhu lebih rendah daripada suhu T_p. Model Lompatan Julat Pembolehubah dan model Lompatan Polaron Kecil Adiabatik sangat berpadanan bagi suhu tinggi dan tenaga pengaktifan keadaan ketumpatan, suhu debye dan frekuansi fonon dapat dianggarkan. Ini menunjukkan tenaga pengaktifan semua sampel adalah dalam julat ~30 meV dan ~180 meV. Pengukuran magnetorintangan menunjukkan nisbah magnetorintangan meningkat dengan penurunan suhu dan peningkatan kepekatan pendopan. Nilai maksimum magnetorintangan penggantian tapak La adalah lebih tinggi berbanding penggantian tapak Ba dan Mn. Nilai MR tertinggi adalah 64.49% pada 1 Tesla diperolehi oleh sampel $(La_{1-x}Nd_x)_{1/2}Ba_{1/2}MnO_3$ (x=1) diukur pada 150 K. Semua sampel menunjukkan terdapatnya kawasan-kawasan magnetorintangan medan rendah (MRMR) dan magnetorintangan medan tinggi (MRMT) kecuali sampel $(La_{1-x}Nd_x)_{1/2}Ba_{1/2}MnO_3$. Nisbah MRMR berkurang dengan meningkatnya suhu. Mikrograf Mikroskop Electron Imbasan (SEM) menunjukkan saiz butiran mengecil dan paras keporosan meingkat dengan peningkatan kandungan dopan yang mana boleh dilihat dalam semua sampel kecuali sampel $La_{2/3}(Ba_{1-x}Pd_x)_{1/3}MnO_3$.

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I certify that an Examination Committee has met on 5th May 2006 to conduct the final examination of Huda Abdullah on her Doctor of Philosophy thesis entitled "Electrical And Magnetoresisitive Properties of Ag-Co/Cu-Fe Thin Films and Bulk Rare-Earth Manganese Perovskite (Ln-Ba-Mn-O)" in accordance with Universiti Pertanian Malaysia (Higher Degree) Act 1980 and Universiti Pertanian Malaysia (Higher Degree) Regulations 1981. The Committee recommends that the candidate be awarded the relevant degree. Members of the Examination Committee are a follows:

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DECLARATION

I hereby declare that the thesis is based on my original work except for quotations and citations, which have been duly acknowledged. I also declare that it has not been previously or concurrently submitted for any other degree at UPM or other institutions.

_____

HUDA BINTI ABDULLAH

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