UNIVERSITI PUTRA MALAYSIA

STRUCTURAL, MAGNETIC, ELECTRICAL AND MAGNETOTRANSPORT PROPERTIES OF (La,Pr)1-x(Sr,Ba)xMnO3 BULK, SINGLE AND BI-LAYER THIN FILMS

ALBERT GAN HAN MING

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By

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Abstract of thesis presented to the Senate of Universiti Putra Malaysia in fulfillment of the requirement for the degree of Master of Science

STRUCTURAL, MAGNETIC, ELECTRICAL AND MAGNETOTRANSPORT PROPERTIES OF $(La,Pr)_{1-x}(Sr,Ba)_xMnO_3$ BULK, SINGLE AND BI-LAYER THIN FILMS

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Colossal magnetoresistance (CMR) compound which exhibit large magnetoresistance value associated with its ferromagnetic-paramagnetic phase transition gain interest from researchers since 1950s. Large drop in resistivity in CMR material at very low magnetic field (0-0.1T) at low temperature (80K) gained further attentions from researchers. This low field magnetoresistance effect can be altered by grain size distribution. Fabrication and characterization of CMR thin film have been done in recent years to study the possibility in various application. Magnetic properties of thin film can be altered by introducing a pinning layer for bilayer film. Very limited report of coupling and stacking sequence of two CMR layer can be found. In this work, several investigation have been done. Effect of various average cation size of rare earth element and alkaline earth element at A-site towards physical properties in $(La,Pr)_{0.67}(Sr,Ba)_{0.33}MnO_3$ system have been studied. $La_{0.67}Sr_{0.33}MnO_3$(LSMO), $Pr_{0.67}Sr_{0.33}MnO_3$(PSMO), $La_{0.67}Ba_{0.33}MnO_3$(LBMO), and $Pr_{0.67}Ba_{0.33}MnO_3$(PBMO) were synthesized by conventional solid state reaction route. Sub-micron grains were obtained for the bulk samples. Transformation from hexagonal to orthorhombic crystal structure was observed when La^{3+} was replaced by Pr^{3+}. However, replacement of Sr^{2+} by Ba^{2+} in the compound only caused different microstructure formation. The difference in electrical, structural and magnetic properties in comparison to bulk samples are due to the difference in average cation size in A-site. T_p observed are >300 K for LSMO, 286 K for PSMO, 256 K for LBMO while PBMO shows T_p at 182 K and 150 K. Two T_p values in PBMO are due to the existing of core shell effect contributed by large difference in ionic size between rare earth and alkaline earth element. T_c observed for PSMO and PBMO are at 301 K and 184 K respectively. However, T_c of LSMO and LBMO were higher than 320 K similar as reported by other researchers. LSMO and PSMO were deposited on corning glass, MgO (100) and fused silica substrate by pulsed laser deposition technique (PLD). Grains obtained are in nano size and agglomerate in "island" like formation. Nano size cracks was observed due to difference in coefficient of thermal expansion between

sample and substrate. Crystal structure retain upon converted into thin film of thickness ~2 μm. Lattice strain induced from the lattice mismatch between sample and substrate affected Mn-O-Mn octahedral bond angle and bond distance, affected metal-insulator transition temperature in each system. Weak ferromagnetic behavior below T_c observed in PSMO-F can be due to the extremely high value of lattice strain induced. Bilayer thin film was synthesize by coupling LSMO and PSMO in different stacking sequences on top of corning glass, MgO (100) and fused silica. Larger grain size in bilayer film is due to the greater diffusion at second deposition. Lattice strain observed in bilayer system is dependent on the stacking sequence of crystal structure of individual film. The observed T_p of the top layer does not change much but curie temperature of top layer seemingly mimic to buffer layer due to magnetic pinning effect. Enhancement of magnetoresistance in bilayer film might due to the increase of disorder in bilayer system. $Pr_{0.67}Sr_{0.33}MnO_3$ with $La_{0.67}Sr_{0.33}MnO_3$ as buffer layer, deposited on MgO (100) showed highest LFMR value which is -14.4% at 80 K and 0.1 T whereas the LFMR value at room temperature (300K) is -0.9%. CMR material can be used for low/high field magnetic field sensing device, land mine detector (Roul *et a*l., 2001), as well as automotive sensors (NXP Semiconductors, 2006)

Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia Sebagai memenuhi keperluan untuk ijazah Master Sains

SIFAT-SIFAT STRUKTUR, MAGNET, ELEKTRIK DAN PENGANGKUTAN MAGNETO UNTUK $(La,Pr)_{1-x}(Sr,Ba)_xMnO_3$ DALAM BENTUK PUKAL, FILEM NIPIS DAN DWI LAPISAN

Oleh

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Bahan dengan magnetorintangan yang besar telah menarik perhatian penyelidik-penyelidik sejak tahun 1950 terutamanya keupayaan bahan tersebut dalam pertukaran sifat magnet daripada feromagnet kepada paramagnet. Pada suhu yang rendah (80K), rintangan bahan tersebut boleh mengurang dalam kadar yang besar hanya dengan applikasi medan magnet yang rendah (0-0.1T). Sifat magnetorintangan pada suhu yang rendah ini boleh dipengaruhi oleh perubahan saiz purata butiran. Pembuatan dan pencirian filem nipis yang diperbuat daripada bahan magnetorintangan tersebut telah dijalankan oleh penyelidik-penyelidik untuk mengkaji penggunaanya dalam kehidupan kita. Sifat magnet dalam filem nipis boleh diubahsuai dengan memendapkan filem nipis ke atas lapisan filem nipis yang lain.Walaubagaimanapun laporan mengenai gandingan dan turutan dua filem yang berlainan dalam pembuatan dwi lapisan filem nipis adalah jarang. Dalam pengkajian ini, beberapa siasatan telah dibuat. Kesan terhadap sifat fizik dalam sistem $(La,Pr)_{0.67}(Sr,Ba)_{0.33}MnO_3$ dengan penggunaan saiz kation yang berlainan di bahagian A telah dikaji. $La_{0.67}Sr_{0.33}MnO_3$(LSMO), $Pr_{0.67}Sr_{0.33}MnO_3$(PSMO), $La_{0.67}Ba_{0.33}MnO_3$(LBMO), dan $Pr_{0.67}Ba_{0.33}MnO_3$(PBMO) diperbuat dengan kaedah tindak balas keadaan pepejal konvensional dan saiz bijiran dalam sub-mikron telah diperolehi. Sistem hablur mengalami transformasi dari heksagon kepada otorombik apabila La^{3+} diganti dengan Pr^{3+}. Tetapi, penggantian Sr^{2+} dengan Ba^{2+} hanya mengakibatkan mikrostruktur yang berlainan. Sifat elektrik, struktur dan magnet yang berlainan dalam sempel adalah disebabkan oleh perbezaan purata saiz kation yang berlainan di bahagian A. T_p yang diperhatikan adalah >300K untuk LSMO, 286K untuk PSMO, 256K untuk LBMO manakala PBMO menunjukkan dua T_p di 182K dan 150K masing masing. Dua nilai T_p yang ditunjuk oleh PBMO adalah disebabkan oleh sifat shell dan teras yang berlainan. Ini adalah kerana perbezaaan saiz ion yang besar antara unsur nadir bumi dan unsur alkali bumi. PSMO dan PBMO menunjukkan T_c pada suhu 301K dan 184K manakala nilai T_c yang ditunjukkan oleh PSMO dan PBMO adalah

lebih tinggi daripada suhu 320K. LSMO dan PSMO telah ditukar menjadi filem nipis berlapis tunggal dan dwi lapisan dengan teknik mendapan dedenyut laser (PLD) ke atas kaca corning, MgO(100) dan silika lakur. Bijiran yang didapati adalah dalam saiz nano dan menggumpal antara satu sama lain. Retakan dalam saiz nano didapati dalam filem nipis yang disebabkan oleh pengembangan terma yang berlainan antara sampel filem dan substrat. Sistem hablur tetap sama walaupun sempel dalam bentul filem nipis yang ketebalannya ~2µm. Regangan kekisi diakibatkan daripada ketidakseragaman kekisi antara filem dan substrat mempengaruhi sudut dan jarak antara Mn-O-Mn yang berbentuk lapan dan seterusnya menpengaruhi suhu transformasi logam-penebat dalam sistem-sistem. Sifat feromagnetik yang lemah pada suhu di bawah T_c di sempel PSMO-F adalah disebabkan oleh regangan kekisi yang lebih tinggi. Filem dwi lapisan telah pun dihasilkan dengan LSMO dan PSMo dalam turutan mendapan yang berlainan di kaca corning, MgO(100) dan silika lakur. Saiz bijiran yang lebih besar dalam filem dwi lapisan adalah disebabkan oleh resapan yang lebih besar antara bijiran pada masa pemendapan yang kedua. Regangan kekisi yang didapati dalam sistem dwi lapisan adalah bergantung kepada turutan dalam mendapan filem-filem yang mempunyai sistem hablur yang berlainan. T_p untuk filem pada lapisan atas tidak banyak berubah manakala suhu curie dari filem lapisan atas seolah-olah meniru daripada filem di lapisan bawah. Ini adalah disebabkan oleh kesan penyematan magnetik. Sifat magnetorintangan dalam dwi lapisan yang lebih kuat mungkin juga disebabkan oleh kecelaruan yang lebih tinggi dalam sistem. $Pr_{0.67}Sr_{0.33}MnO_3$ yang mendap atas $La_{0.67}Sr_{0.33}MnO_3$ di substrat MgO(100) telah menunjukkan magnetorintangan yang paling besar iaitu -14.4% pada suhu 80K dengan medan magnet 0.1T. Bahan yang mempersembahkan magnetorintangan boleh digunakan sebagai sensor magnet, pengesan ranjau letupan darat, dan juga sensor kereta.

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LIST OF ABBREVIATIONS

AE	Alkaline Earth Element
RE	Rare Earth Element
%MR	Percentage of Magnetoresistance
MR	Magnetoresistance
CMR	Colossal Magnetoresistance
LFMR	Low Field Magnetoresistance
SEM	Scanning Electron Microscope
FESEM	Field Emission Electron Microscope
XRD	X-ray Diffraction
Mn-O	Bond distance between Manganese Ion and Oxygen Ion.
Å	Angstrom
%	Percentage
K	Kelvin
T_c	Curie Temperature
T_p	Metal-Insulator Transition Temperature
ICSD	Inorganic Crystal Structure Database
SSMO	$Sm_{0.55}Sr_{0.45}MnO_3$
NDMO	$Nd_{0.55}Sr_{0.45}MnO_3$

CHAPTER 1

INTRODUCTION

1.1 Magnetoresistance Material

Several types of magnetoresistanc(MR) effect and these include Ordinary MR, Anisotropic MR, Giant MR, Tunneling MR and Colossal MR. All these MR effects were exhibited through different combinations of element where the resistivity droped with certain applied magnetic field strength. Colossal magnetoresistance (CMR) which was known to exist since 1950 gained interest from researchers due to its large magnetoresistance value associated with its ferromagnetic-paramagnetic phase transition. Apart from this, low field magnetoresistance effect where larger drop in resistivity in CMR material at very low magnetic field (0-0.1T) at low temperature gained further attentions because this magnetic field strength region is suitable for application in magnetic reading devices (Ramirez *et al*, 1997). Most of the manganite compound followed the general formula $RE_{1-x}AE_xMnO_3$ where RE= trivalent element, AE=divalent element. The electric and magneto transport properties at temperatures lower than T_c/T_p are mainly contributed by double exchange mechanism. At low temperature, compound in ferromagnetic state have most of the electron spin arranged in the same direction. Electron from the 3d orbital of Mn^{3+} can easily hop to Mn^{4+} through oxygen atom thus creating the movement of electron in the structure. This double exchange (DE) mechanism can easily be affected by the alignment of the electron spin and thus applied magnetic field could smoothen the electron hopping process and lowering down the resistivity value. However, double exchange mechanism itself cannot describe the conducting phenomena in CMR compound. Above T_c, CMR compound turns into paramagnetic state where the electron spin fluctuated and disordered. DE mechanism is then weakened. Jahn-Teller theory was introduced to mention the conducting effect at above T_c with the coexistence of Hund's coupling effect. Electrons in the structure can hop when MnO_6 octahedral remove the degeneracy by displacing from its original position.

Thin film gained interest from researchers due to its potential application. Upon converting bulk manganite into thin film, several factors like type of substrate used, annealing temperature, synthesis technique (Fors *et al*.,2004; Fang *et al*., 2011; Malisa and Ivanov, 2005), film thickness and etc have to be taken into consideration. These factors affect the physical properties like microstructure formation and thus electro/magneto transport properties. However, there are still a lot more investigation yet to be done on these manganite materials.

1.2 **Problem Statement**

Taran *et al*. (2006) prepared single layer and bilayer thin film of $La_{0.67}Sr_{0.33}MnO_3$ (SL1), $La_{0.67}Ca_{0.33}MnO_3$ (SL2) and $La_{0.67}Sr_{1.33}MnO_4$ (SL3) on $SrTiO_3$ (001) substrate by RF (radio frequency) magnetron sputtering technique. Large enhancement of magnetoresistance at 1.2T field from 8% (SL1) and 35% (SL2) to 12%(SL1/SL3) and 50%(SL2/SL3). T_p reported shifted towards lower temperature (370 K for SL1 and 295 K for SL1/SL3) due to the increase of disorder and strain effect in bilayer film. The same thing happen for SL2 and SL2/SL3 where T_p drops from 248 K to 225 K. This phenomena is due to strain induced from unequal structure as reported. SEM micrograph of single layer film system showed average grain size around ~100 nm. Increase of MR in bilayer system was due to the increase in disorder. Park *et al*. (2004) also fabricate bilayer $La_{0.8}Sr_{0.2}Mno_3/La_{0.8}Ca_{0.2}MnO_3$ by rf sputtering technique. T_p of LSMO and LCMO reported are about the same which is at 230 K but shifted to 280 K in bilayer form. Increased in T_c also reported in bilayer film as T_c of bilayer is about 280 K while T_c of LSMO and LCMO are found 260 K and 230 K respectively. Effect of lattice strain in $La_{0.8}Sr_{0.2}MnO_3/La_{0.8}Ca_{0.2}MnO_3$ bilayer grown on $LaAlO_3$ (001) was studied by Prokhorov *et al.* (2007). Lattice parameter of the top layer, $La_{0.8}Sr_{0.2}MnO_3$ is dependent on the buffer layer/substrate's c-axis as reported. T_p shifted to higher temperature where T_p is of single layer film $La_{0.8}Sr_{0.2}MnO_3$ and $La_{0.8}Ca_{0.2}MnO_3$ reported are very close at about 230 K while bilayer film is at 280 K. Changes in lattice parameter C for $La_{0.8}Sr_{0.2}MnO_3$ in bilayer improve magnetic and electronic properties. However, not much work and studies on the microstructure properties in bilayer film. Very fews report can be found for coupling effect and stacking sequences effect of two type of manganite film. So, investigation in certain area is important such as:

1. The effect of average cation radius changed in $RE_{1-x}AE_xMnO_3$ by substitution of rare earth element or alkaline earth element in structural, electrical and magnetotransport properties.

2. The substrate effect towards structural, electrical and magnetotransport properties of CMR material upon converted into thin film.

3. The effect of thin film coupling by LSMO (T_c > 300K) and PSMO (T_c <300K) towards structural, electrical and magnetotransport properties as well as influence brought by stacking sequences.

1.3 Objective

In bulk system, varied rare earth element (La^{3+},Pr^{3+}) and alkaline element (Sr^{2+}, Ba^{2+}) in manganese compound were studied. All CMR compounds followed the general formula $RE_{0.67}AE_{0.33}MnO_3$ (RE: rare earth element; AE: alkaline earth element) to fix the ratio of Mn^{3+}/Mn^{4+} so that comparison can be made. Single layer thin film was fabricated on various substrate to study the substrate effect. The bi-layer thin film coupling by $La_{0.67}Sr_{0.33}MnO_3$ which showed high phase transition temperature (>300K) and $Pr_{0.67}Sr_{0.33}MnO_3$ with low transition (<300K) were interested to study by varying the stacking sequence. In this work, the objective is:

1. To fabricate $La_{0.67}Sr_{0.33}MnO_3$, $La_{0.67}Ba_{0.33}MnO_3$, $Pr_{0.67}Sr_{0.33}MnO_3$, and $Pr_{0.67}Ba_{0.33}MnO_3$ bulk samples via solid state reaction method and characterize in structural, electrical, and magnetotransport properties.

2. To fabricate single layer thin film of $La_{67}Sr_{0.33}MnO_3$, $La_{0.67}Ba_{0.33}MnO_3$, $Pr_{0.67}Sr_{0.33}MnO_3$, and $Pr_{0.67}Ba_{0.33}MnO_3$ deposited on amorphous (corning glass and fused silica) and single crystal (MgO 100) substrate via pulsed laser deposition method and characterize in structural, electrical, and magnetotransport properties.

3. To fabricate bi-layer thin film of $La_{0.67}Sr_{0.33}MnO_3$ and $Pr_{0.67}Sr_{0.33}MnO_3$ by varied the stacking sequence on amorphous (corning glass and fused silica) and single crystal (MgO 100) substrate via pulsed laser deposition method and characterize in structural, electrical, and magnetotransport properties.

1.4 Thesis Structure

Some literature review and simple theory were showed in Chapters 2 and 3. Solid state sintering technique, pulsed laser deposition technique, the machine and skill used to characterize the structure, microstructure, magnetoresistance, electric and magnetotransport, are explained in Chapter 4 (methodology). Analysis of result and comparisons were showed in Chapter 5 (result and discussion). Last but not least, conclusion was made in chapter 6. References and Appendix were attached at the end of the thesis.

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