UNIVERSITI PUTRA MALAYSIA

STRUCTURAL AND MAGNETOTRANSPORT PROPERTIES OF BULK RARE EARTH BARIUM MANGANITE AND (La, Pr)-Ba-Mn-O SINGLE- AND BI-LAYER THIN FILMS

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By

WONG JEN KUEN

Thesis Submitted to the School of Graduate Studies, Universiti Putra Malaysia, in Fulfillment of the Requirement for the Degree of Master of Science

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To My Family Members and Friends.....

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

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September 2011

Chairman : Lim Kean Pah, PhD

Faculty : Science

Magnetoresistance based sensor had been long used in magnetic field sensing application. Higher sensitivity and smaller in size is essential to keep up with the increasing of magnetic storage density. In this work, magnetotransport and magnetic properties of manganites are studied in both bulk and thin films. The influence of different rare earth cation in Ln site of bulk $Ln_{0.67}Ba_{0.33}MnO_3$ (Ln= La, Ce, Pr, Nd, Sm, Gd, Dy and Er) compound synthesized via conventional solid state reaction route was studied. All substituted compound are in single phase except Ce, Dy and Er which are in oxide mixture due to differences in enthalpy of fusion. The crystal system undergoes transformation from orthorhombic to tetragonal when larger (La) cation was substituted by smaller (Gd) cation into Ln site. Substitution of smaller cation at Ln site increases the resistivity and shifts the phase transition temperature,T_P and Curie temperature,T_C to lower temperature. At room temperature, the ferromagnetic $La_{0.67}Ba_{0.33}MnO_3$ (LBMO) undergoes magnetic dilution (glassy magnetic state) and became paramagnetic due to

spin pinning effect when substituted by smaller rare earth cation. The highest room temperature negative %MR was given by $Gd_{0.67}Ba_{0.33}MnO_3$ (GBMO) with -34.09% in 10kG. Substitution of smaller rare earth element into Ln site could enhance the %MR but results in the formation of complicated glassy magnetic state. The work then extended by fabrication of single and bi-layer (LBMO and/or PBMO) thin films through pulsed laser deposition technique on different type of substrate. Upon converted into thin film, the crystal systems remain orthorhombic. The unit cell of both LBMO and PBMO single layer thin films experience positive misfit due to lattice strain induced from lattice misfit between film and substrate. For bi-layer thin films, the lattice misfit is sequence dependent where negative misfit in PB/LB coupling and positive misfit in LB/PB coupling. The resistivity is higher for single layer thin film having more and larger nanocracks when deposited on substrate with smaller coefficient of thermal expansion. The resistivity of bi-layer thin films grown on amorphous substrate is lower than single layer thin films and is contrary on MgO substrate. T_P shifted to lower temperature (<80K) in thin film form. The room temperature magnetic properties of single layer thin films were substrate dependent where PBMO growth on amorphous substrates was more ferromagnetic and vice versa for LBMO. However, room temperature magnetic properties between LB/PB and PB/LB bi-layer films are different. The magnetizations are relatively smaller as compared to single layer thin films (LBMO or PBMO) due to magnetic pinning effect. Their magnetization values were substrate dependent as well as stacking sequence on amorphous substrate but not for single crystal substrate. Typical polycrystalline manganites behavior was observed in all thin film samples where %MR further increase at lower temperature. This shows the extrinsic CMR behavior originated from grain boundary is stronger in thin films compared to bulk. Indeed, conversion from

bulk to thin film can enhance %MR value. Single layer LBMO thin films growth on amorphous substrate shows low field magnetoresistance (LFMR) effect and further enhancement in bi-layer films but not on single crystal MgO substrate. Improvement of %MR value of -28.8% from bulk LBMO to -35.90% (LBMO-FS), -34.60% (LBMO-CG) and -31.40% (LBMO-M) were observed at temperature of 80K in 10kG. The highest negative %MR and LFMR value obtained in this work was PBMO-M (-50.00%) and PB/LB-FS (-12.40%) at temperature of 80K in 10kG respectively whereas the highest room temperature negative %MR in 10kG was given by bulk GBMO (-34.09%).

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SIFAT-SIFAT STRUKTUR DAN PENGANGKUTAN MAGNETO NADIR BUMI BARIUM MANGANAT DALAM BENTUK PUKAL DAN FILEM-FILEM NIPIS (La,Pr)-Ba-Mn-O BERLAPIS TUNGGAL DAN DWI LAPISAN

Oleh

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Sensor magnetorintangan telah lama digunakan dalam aplikasi pengesanan medan magnet. Sensitiviti yang lebih tinggi dan saiz yang lebih kecil adalah sangat penting dengan pertambahan ketumpatan simpanan magnet. Dalam penyelidikan ini, pengangkutan magneto dan sifat-sifat kemagnetan manganat dikaji dalam bentuk pukal dan filem nipis. Pengaruh daripada kation nadir bumi yang berbeza di tapak Ln dalam sebatian $Ln_{0.67}Ba_{0.33}MnO_3$ (Ln= La, Ce, Pr, Nd, Sm, Gd, Dy dan Er) disintesis dengan kaedah tindak balas keadaan pepejal yang konvensional telah dikaji. Semua sebatian yang disubstitusi menunjukkan fasa tunggal kecuali Ce, Dy dan Er yang wujud dalam campuran oksida disebabkan oleh perbezaan dalam enthalpi lakuran. Sistem hablur mengalami transformasi daripada ortorombus kepada tetragon apabila kation (La) yang lebih besar digantikan dengan kation (Gd) yang lebih kecil ke dalam tapak Ln. Penggantian kation yang lebih kecil meningkatkan keringtangan dan menggeserkan suhu peralihan fasa,T_P dan suhu Curie,T_C ke suhu yang lebih rendah. Pada suhu bilik,

feromagnet $La_{0.67}Ba_{0.33}MnO_3$ (LBMO) mengalami pencairan magnet (keadaan magnetik yang rumit) dan menjadi paramagnet akibat kesan sematan spin yang disebabkan oleh kation nadir bumi yang lebih kecil. %MR negatif yang tertinggi pada suhu bilik diberi oleh GBMO (-34.09%) dalam 10kG. Penggantian kation nadir bumi yang lebih kecil ke dalam tapak Ln boleh meningkatkan %MR tetapi mengakibatkan pembentukan keadaan magnet yang merumitkan. Kajian ini kemudian dilanjutkan dengan menyediakan filem nipis (LBMO dan/atau PBMO) berlapis tunggal dan dwi lapisan dengan teknik mendapan dedenyut laser (PLD) pada jenis substrat yang berbeza. Setelah ditukar menjadi filem nipis, struktur hablur masih kekal ortorombus. Sel unit daripada kedua-dua jenis filem nipis LBMO dan PBMO berlapis tunggal mengalami tidak seragam positif disebabkan regangan kekisi yang terhasil daripada tidak seragaman kekisi antara filem dan substrat. Untuk filem nipis dwi lapisan, tidak seragaman kekisi adalah bergantung kepada urutannya dimana tidak seragam negatif dalam gandingan PB/LB dan tidak seragam positif dalam gandingan LB/PB. Keringtangan adalah lebih besar untuk filem nipis berlapis tunggal dengan retakan bersaiz nano yang lebih banyak dan lebih besar apabila dimendap ke atas substrat dengan pekali pengembangan terma yang lebih kecil. Sebagai perbandingan, keringtangan filem-filem nipis dwi lapisan tumbuh di atas substrat amorfus adalah lebih rendah daripada filem-filem nipis berlapis tunggal dan adalah bersongsangan pada substrat MgO. T_P beranjak ke suhu yang lebih rendah (<80K) apabila bertukar ke bentuk filem nipis. Sifat-sifat magnet suhu bilik filem-filem yang berlapis tunggal adalah bergantung kepada substrat yang digunakan dengan pertumbuhan PBMO pada substrat amorfus adalah lebih feromagnet dan adalah bersongsangan untuk LBMO. Walau bagaimanapun, sifat-sifat magnet pada suhu bilik antara filem LB/PB dan PB/LB dwi lapisan adalah berlainan antara satu sama lain dan

lebih kecil berbanding dengan filem-filem nipis berlapis tunggal (LBMO atau PBMO) akibat kesan sematan spin. Nilai-nilai kemagnetan adalah bergantung kepada substrat yang digunakan dan susunan urutan pada substrat amorfus tetapi bukan untuk substrat hablur tunggal. Peranan yang biasa untuk polihabluran manganat telah diperhatikan dalam semua sampel filem nipis dimana %MR adalah bertambah berterusan pada suhu yang lebih rendah. Oleh demikian, peranan CMR ekstrinsik yang berasal dari sempadan butiran adalah lebih kuat di dalam filem-filem nipis berbanding dalam bentuk pukal. Justeru itu, penukaran daripada bentuk pukal ke filem nipis boleh meningkatkan nilai %MR. Filem nipis LBMO berlapis tunggal yang ditumbuhkan pada substrat amorfus menunjukkan kesan magnetorintangan medan rendah (LFMR) dan meningkat dalam filem-filem nipis dwi lapisan tetapi bukan pada substrat hablur tunggal MgO. Manakala, peningkatan nilai %MR -28.8% daripada bentuk pukal LBMO kepada -35.90% (LBMO-FS), -34.60% (LBMO-CG) dan -31.40% (LBMO-M) telah diperhatikan pada suhu 80K dalam 10kG. Nilai %MR dan LFMR negatif tertinggi masing-masing diperolehi dalam kajian ini ialah PBMO-M (-50.00%) dan PB/LB-FS (-12.40%) pada suhu 80K dalam 10kG manakala %MR negatif yang tertinggi pada suhu bilik dalam 10kG diberi oleh GBMO (-34.09%) dalam bentuk pukal.

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DECLARATION

I declare that the thesis is my original work except for quotations and citations which have been duly acknowledged. I also declare that it has not been previously, and is not concurrently, submitted for any other degree at Universiti Putra Malaysia or at any other institution.

WONG JEN KUEN

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