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Preparation and Properties of Polycrystalline and Epitaxial Manganite Films for Pulsed Magnetic Field Application

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Introduction

During last decade manganese oxides, called manganites, have received considerable attention due to possibilities to change their properties under temperature, magnetic and electric fields action or optical excitation. The physical properties of polycrystalline sintered manganites, single crystals and thin films were widely investigated and discussed in the literature. The electrical and magnetic properties of thin films are of special interest due to their potential application for the development of spin-electronics devices, such as vertical tunnel junctions, nanostructured devices and magnetic field sensors. It is very important to guide technological processes during preparation of thin films in order to obtain samples with special requirements. The electrical and magnetic properties of manganite films are closely related to their composition, crystallinity and epitaxy, oxygen content, i.e. to the characteristics that strongly depend on the deposition conditions [1,2]. The films prepared for pulsed magnetic field applications, namely for the development of magnetic field sensors, have to satisfy several requirements, the main of which are the following: no magnetoresistance saturation at high magnetic fields, high-speed responsiveness, and sensitivity independence to the direction of magnetic field.

In this paper, we report on deposition techniques and conditions used for preparation of thin manganite films on which bases pulsed magnetic field sensors were developed.

Experimental

Two deposition techniques were used for manganite films preparation: metal organic chemical vapour deposition (MOCVD), using vertical hot wall injection CVD reactor, and laser deposition. The first method was used for the deposition of monocrystalline and polycrystalline $La_{0.83}Sr_{0.17}MnO_3$ (LSMO) films. In the injection CVD reactor, which was used in this method, films can be deposited on substrates up to 2 inches in diameter. The principal scheme of this reactor is presented in Fig.1. The injector injects microdoses (a few microlitres) of an organic solution containing a dissolved mixture of organometallic precursors. After flash evaporation of a microdose, the resulting vapour mixture is transported by $Ar+O_2$ gas towards the heated substrate. Substrate's temperature is kept at 750 – 825 ^{0}C. The injector is a computer-driven, high speed and precision electromagnetic valve operating in repetitive pulsing. There are a lot of possibilities to vary the precursor delivery rate and the growth rate (pulse duration, injection frequency, pressure in the solution reservoir, solution concentration). The epitaxial LSMO films were grown on $LaAlO_3$ (LAO), $SrTiO_3$ (STO) and $NdGaO_3$ (NGO)

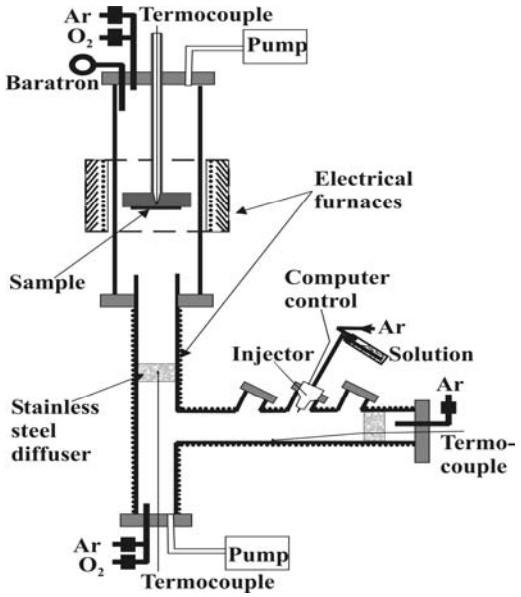

Fig. 1. Injection CVD reactor

substrates. The thickness of the obtained films was in the range from 4 nm up to 200 nm. The growth rate of the films was approximately 0.6 μm/h. After deposition the films were cooled to room temperature in oxygen (760 torr). Details of epitaxial growth of the films are described in [3]. The polycrystalline films were deposited on lucalox substrates. Deposition conditions are presented in Table 1. The thickness of the films was 140 – 200 nm.

Table 1. Deposition conditions for polycrystalline LSMO films

Substrate temperature	650-825 ^{0}C
Evaporator temperature	290 ^{0}C
Total gas flow rate ($Ar+O_2$)	102 l/h
Total pressure	5 torr
O_2 pressure	1.6 torr
Precursors	$La(tmhd)_3$, $Sr(tmhd)_2$, $Mn(tmhd)_3$
Solvent	monoglyme
Solution concentration	0.03 mol/l (La+Sr)
Solution composition	$La_{0.78}Sr_{0.22}Mn_{0.73}$
Injection frequency	2 Hz
Mass of injected microdose	3 mg

The second method, laser deposition, was used for deposition of epitaxial and polycrystalline $La_{0.67}Ca_{0.33}MnO_3$ (LCMO) films onto NGO and lucalox substrates, respectively. On-axis pulsed laser deposition technique using a Nd^{3+}:YAG laser, operating at a single (λ= 1064 nm, first harmonic) and doubled frequency mode (λ= 532 nm, second harmonic) was used in this method. Laser pulse energy was chosen to be 50 mJ. The oxygen background pressure was 350 mTorr. After deposition, in-situ annealing was performed at 750 ^{0}C in an oxygen pressure of 500 mTorr for 30 min. The target was prepared by conventional solid state reaction processing. The thickness of these films was 140 – 300 nm.

For the transport measurements, the electrical contacts of the samples were made by thermal deposition of Ag, using a Cr sub-layer. Cr film fulfils a function of adherent film among LS(C)MO and Ag films, which offers a good soldering with wires. Finally, a thermal treatment at 400 ^{0}C for 20 min in an O_2 atmosphere was carried out in order to reduce the contact resistance. Therefore, all measurements were carried out using only two electrical contacts. It enabled to reduce parasitic signals during measurements at high pulsed magnetic fields. The electrical contacts of the samples were spaced by 20 μm gap. The obtained 1 mm long and 1 mm wide samples were soldered to bifilar twisted wires.

The crystallinity of obtained films was examined by X-ray diffraction (XRD) analysis of θ-2θ scans and by reflection high-energy electron diffraction (RHEED). Scanning electron microscope (SEM) and atomic force microscopy (AFM) were used to study the surface morphology of the samples.

The magnetoresistance (MR=[R(0)-R(B)]/R(0)) of polycrystalline and epitaxial manganite thin films was studied at room temperature in high pulsed magnetic fields up to 35 T. The compact pulsed magnetic field generator [4,5] was used for the generation of half-period sinus-shaped strong magnetic field pulses of 1-2 ms in duration and with amplitudes up to 45 T. The structure of measurements is shown in Fig. 2.

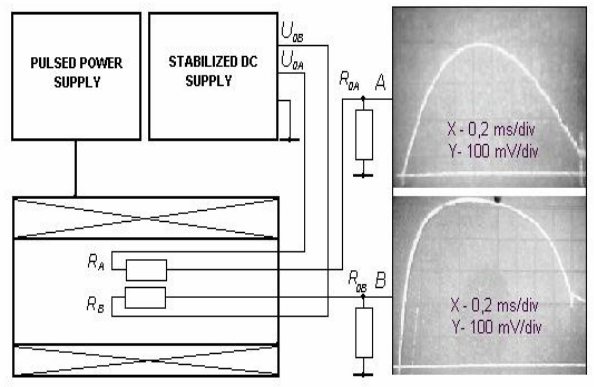

Fig. 2. Measurements of magnetoresistance of polycrystalline (channel A) and epitaxial (channel B) manganite thin films in pulsed magnetic field

Two thin manganite thin films, one polycrystalline with the resistance of R_A and another epitaxial with the resistance R_B, were placed in central area of the pulsed coil connected with pulsed power supply. Pulsed power supply block includes the adjustable high voltage power supply up to 5000V, capacitor bank of 5000μF and pulsed thyristor switch. Electric energy was transformed into magnetic energy discharging the capacitor bank through the pulsed coil, and a sinus shaped magnetic field pulse was generated. For transport measurements voltage from stabilized DC power supply was applied to in series connected manganite films and ballast resistors R_{0A}, R_{0B}, The response of manganite films to magnetic pulse was registered simultaneously with two memorized oscilloscopes. The responses of polycrystalline and epitaxial films to sinus shaped magnetic pulse are presented in Fig.2 as images at channel A and channel B, respectively.

Results and discussion

Films grown on LAO, STO and NGO substrates were obtained as good quality epitaxial films, and on the XRD θ-2θ scan profiles only a narrow peak of LSMO was observed. θ-2θ scan of LSMO/LAO 20 nm thickness film is presented in Fig.3. Films deposited on lucalox substrates have a polycrystalline, slightly textured structure. The RHEED patterns recorded from these films have a short arc shape spots with advantage orientation {111} perpendicular to the substrate surface.

Temperature dependencies of specific resistance $\rho(T)$ of prepared films are shown in Fig.4. Curves 1 and 2 correspond to the $\rho(T)$ of the LSMO films grown by MOCVD on monocrystalline and polycrystalline substrates, respectively. The substrate material undoubtedly influences the electrical properties of the films. The electrical transport measurements show the typical for manganites metal-insulator transition with the peak resistivity of ~10 mΩcm at temperature T_m =320 K. The peak resistivity of these films was about ~1130 mΩcm

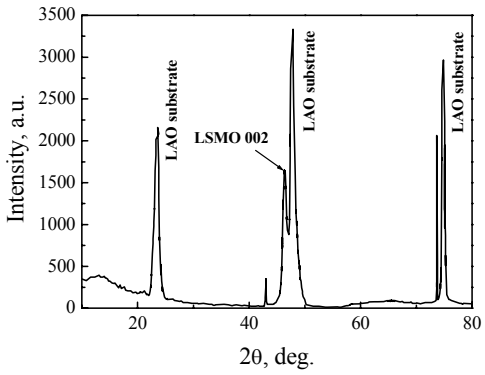

Fig. 3. X-ray diffraction pattern of 20 nm thickness LSMO film grown on LAO substrate

at temperature T_m =220 K. At low temperature resistivity of epitaxial and polycrystalline films was 0.5 mΩcm and 570 mΩcm, respectively. The high resistivity (curve 2) and shift of the T_m to lower temperatures can be explained by taking into consideration the polycrystalline structure of the film, which consists of grain boundaries (GB) between crystallites surrounded by mesoscopic regions. In this case the resistivity of the film is determined by the resistivity of grain boundaries.

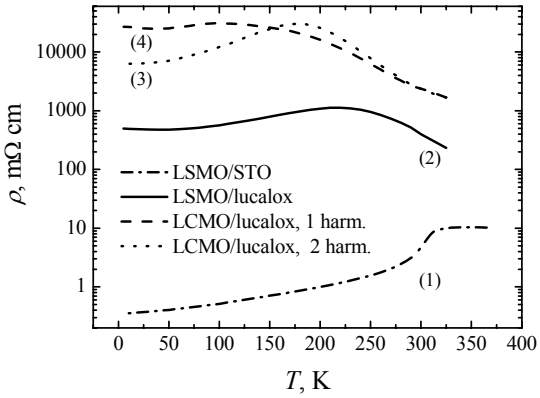

Fig. 4. Specific resistance dependence on temperature of $La_{0.83}Sr_{0.17}MnO_3$ and $La_{0.67}Ca_{0.33}MnO_3$ films prepared by different techniques: (1), (2) –by MOCVD, (3) – by laser deposition 2st harmonic, (4) – by 1st harmonic

LCMO films grown on lucalox substrates by laser deposition technique have only polycrystalline structure. They have high electrical resistivity with peak of 30 Ωcm at temperature about T_m =180K (see Fig.4 curve 3) for films deposited by using second laser harmonic, and with peak of ~31 Ωcm at T_m =100 K (Fig.4 curve 4) for films deposited by the first laser harmonic.

The increase in film resistance and shift of T_m to lower temperatures is also obtained for epitaxial films when film thickness is decreased. Fig. 5 presents the $\rho(T)$ dependence of various thickness epitaxial LSMO films grown on (001) NGO substrate. For 140 nm thickness film the peak of 13 Ωcm is observed at T_m =320K, while for 4 nm thickness film the peak of 182 Ωcm is observed at T_m =210K. Such

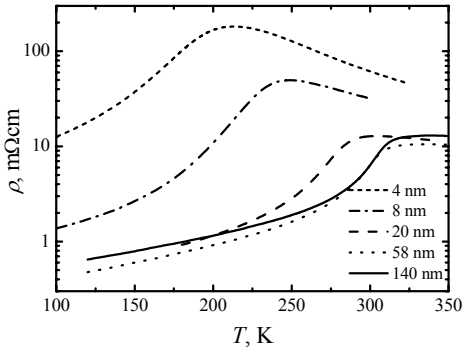

Fig. 5. Specific resistance dependence on temperature of $La_{0.83}Sr_{0.17}MnO_3$ films with different thicknesses prepared by MOCVD technique

behaviour of the resistivity with decrease of film thickness could be probably explained by the existence of two-phases at the interface between the film and substrate.

The surface morphology of prepared films was studied by using scanning electron and atomic force microscopy.

The results of SEM for films obtained by pulsed laser deposition and MOCVD techniques are shown in Fig. 6.

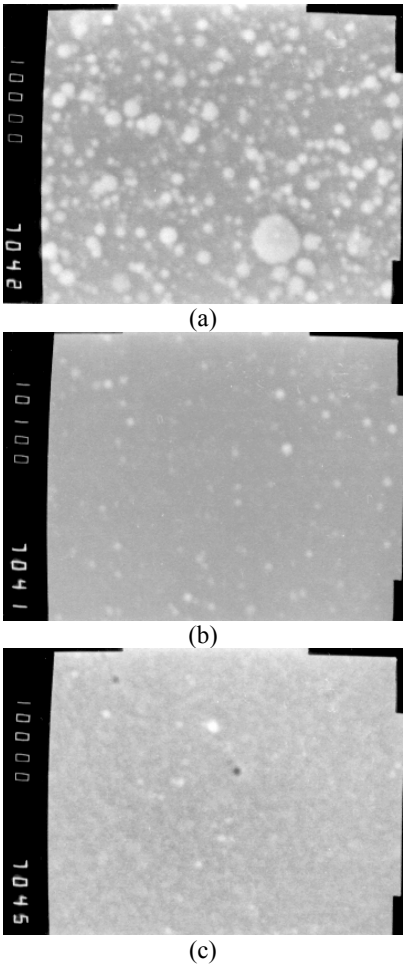

Fig. 6. SEM pictures (magnification 3900x) of manganite films grown by (a) laser deposition 1st harmonic, (b) laser deposition 2nd harmonic, (c) MOCVD

One can see a lot of small drops on the surface of film deposited by the first harmonic of the laser (Fig. 6a). It is because the evaporation in this case occurs from deep places in the target and small drops of substance propagate together with the molecular stream. The films prepared by the second harmonic of the laser have rather smooth surface with few drops in area of mm^2 (Fig. 6b). In opposite, the film, grown by MOCVD, has the smooth surface without any drops (Fig. 6c). The 3D image obtained by AFM for LSMO film grown on NGO substrate is presented in Fig. 7.

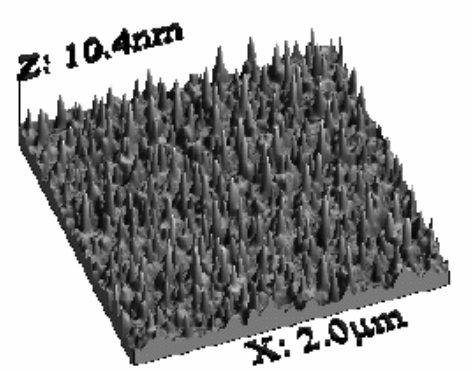

Fig. 7. 3D image obtained by AFM of 20 nm thickness LSMO film grown on NGO substrate

The magnetoresistance (*MR*) of the films grown by different techniques is shown in Fig.8. *MR* was obtained from the film's resistance response to pulsed magnetic fields. For the epitaxial film, the high sensitivity of *MR* in magnetic field lower than 3 T and low sensitivity in high magnetic field is observed. Such behaviour can be attributed to colossal magnetoresistance in bulk perovskite manganites with sharp paramagnetic-ferromagnetic transition. In high magnetic field the whole film is in the ferromagnetic phase and *MR* is only slightly dependent on the magnetic field.

The smaller, but not saturated *MR* was observed for films grown on lucalox substrates. Lower sensitivity for

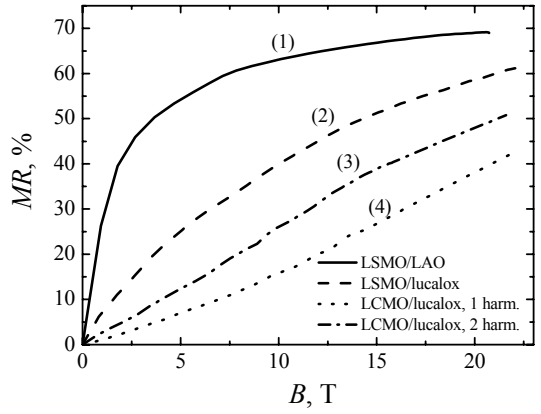

Fig. 8. Magnetoresistance dependence on magnetic field inductance of $La_{0.83}Sr_{0.17}MnO_3$ and $La_{0.67}Ca_{0.33}MnO_3$ films prepared by different techniques: (1), (2) –by MOCVD, (3) – by laser deposition 2st harmonic, (4) – by 1st harmonic

film's grown by the first laser harmonic (curve 4) and highest for the film grown by MOCVD (curve 2) was observed for polycrystalline films. These results demonstrate that, in the case of polycrystalline films, strong magnetic field induced *MR* effect takes place mainly at grain boundaries having vitreous structure and located between crystallites, which are in the conducting ferromagnetic state at room temperature. Therefore, it is possible to vary properties of the *MR* effect in manganites by changing the size and number of these boundaries. This is very important in the design of pulsed high magnetic field sensors.

Conclusions

In conclusion, the pulsed liquid injection MOCVD technique as well as the laser deposition technique allows to growth high quality epitaxial and polycrystalline LCMO and LSMO films. Changing the deposition conditions, substrates, film structure and thickness it is possible to obtain variation of electrical and magnetic properties of the films in very wide range. Increase in polycrystallinity and non-homogeneity of the film's structure leads to increase in specific resistance and decrease of maximum temperature of $\rho(T)$ dependence. The similar behaviour could be obtained decreasing thickness of the film down to several nanometres. For the high pulsed magnetic field sensors development polycrystalline LCMO films exhibiting lower *MR* sensitivity in comparison with epitaxial films, but no saturation effects in high magnetic fields can be successfully used to measure absolute value of the field.

Acknowledgements

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Pateikta spaudai 2005 02 08

V. Stankevič, F. Anisimovas, A. Abrutis, V. Plaušinaitienė, J. Novickij, S. Bartkevičius. Polikristalinių ir epitaksinių manganitų sluoksnių gamybos technologija bei savybės ir jų panaudojimas impulsiniams magnetiniams laukams matuoti // Elektrotechnika ir elektronika. – Kaunas: Technologija, 2005. –Nr. 5(61). – P. 33–37.

Pateikta plonųjų manganitų sluoksnių gamybos technologija ir auginimo sąlygos, siekiant šių sluoksnių savybes panaudoti impulsinio magnetinio lauko jutikliams kurti. Aukštos kokybės epitaksiniai ir polikristaliniai $La_{0.83}Sr_{0.17}MnO_3$ ir $La_{0.67}Ca_{0.33}MnO_3$ sluoksniai buvo užauginti cheminiu gariniu (MOCVD) ir lazeriniu metaloorganinio junginio nusodinimu. Parodyta, kad, keičiant auginimo sąlygas, padėklus, sluoksnių struktūrą ir storį, galima labai plačiame ruože keisti manganitų elektrines ir magnetines savybes. Didinant sluoksnių polikristališkumą ir struktūros netvarkumo laipsnį, padidėja sluoksnio specifinė varža ir pažemėja fazinio virsmo temperatūra. Tokios pat savybės gaunamos, mažinant epitaksinio sluoksnio storį iki kelių nanometrų. Sluoksnių, nusodintų skirtingais metodais, magnetovarža buvo išmatuota iki 35 T magnetiniuose laukuose, naudojant stiprių impulsinių magnetinių laukų generatorių. Nustatyta, jog polikristaliniai sluoksniai, palyginti juos su epitaksiniais sluoksniais, turi keletą pranašumų, kuriant impulsinio magnetinio lauko jutiklius. Nors jų jautris magnetiniam laukui yra mažesnis, bet polikristalinių sluoksnių magnetovarža neįsisotina iki 35 T ir nepriklauso nuo magnetinio lauko krypties. Todėl manganitų polikristaliniai sluoksniai gali būti sėkmingai panaudoti, kuriant stipraus impulsinio magnetinio lauko jutiklius. Il. 8, bibl. 5 (anglų kalba; santraukos lietuvių, anglų, rusų k.)

V. Stankevič, F. Anisimovas, A. Abrutis, V. Plaušinaitienė, J. Novickij, S. Bartkevičius. Preparation and Properties of Polycrystalline and Epitaxial Manganite Films for Pulsed Magnetic Field Application // Electronics and Electrical Engineering. – Kaunas: Technologija, 2005. – No. 5(61). – P. 33–37.

Deposition techniques and conditions used for preparation of thin manganite films on which bases pulsed magnetic field sensors were developed are described. High quality epitaxial and polycrystalline $La_{0.83}Sr_{0.17}MnO_3$ and $La_{0.67}Ca_{0.33}MnO_3$ films are prepared by pulsed liquid injection MOCVD technique and laser deposition. Possibilities to obtain variation in very wide range of electrical and magnetic properties of the films changing the deposition conditions, substrates, film structure and thickness are shown. Increase in polycrystallinity and non-homogeneity of the film's structure leads to increase in specific resistance and decrease of the maximum temperature of $\rho(T)$ dependence. The similar behaviour could be obtained decreasing thickness of epitaxial film down to several nanometres. Magnetoresistance *MR* of films prepared by different techniques and at different conditions was investigated at pulsed magnetic fields up to 35 T. The obtained results showed that polycrystalline films have several advantages in comparison with epitaxial ones for the development of pulsed magnetic field sensors. In spite of lower *MR* sensitivity, polycrystalline films have no *MR* saturation effects in high magnetic fields and can be successfully used to measure absolute value of the fields up to 35 T. Ill. 8, bibl. 5 (in English; summaries in Lithuanian, English, Russian).

В. Станкевич, Ф. Анисимовас, А. Абрутис, В. Плаушинайтене, Ю. Новицкий, С. Барткевичюс. Получение и свойства поликристаллических и эпитаксиальных манганитных пленок с целью использования их для измерений импульсных магнитных полей // Электроника и электротехника. – Каунас: Технология, 2005. – № 5(61). – С. 33–37.

Описана технология выращивания и особенности приготовления тонких манганитных пленок для последующего их применения в качестве датчиков импульсного магнитного поля. Высококачественные эпитаксиальные и поликристаллические $La_{0.83}Sr_{0.17}MnO_3$ и $La_{0.67}Ca_{0.33}MnO_3$ пленки были получены методом MOCVD и импульсного лазерного осаждения. Установлено,что электрические и магнитные свойства манганитных пленок могут быть изменены в широком диапазоне путем изменения условий выращивания пленок, использования различных подложек а также изменением структуры и толщины пленок. Увеличение степени поликристалличности и беспорядочности структуры пленок, приводит к увеличению удельного сопротивления пленок и уменьшению температуры фазового перехода. Магнитное сопротивление пленок, полученных различными методами осаждения, исследовалось в импульсном магнитном поле до 35 Т. Установлено, что для измерения импульсных магнитных полей поликристаллические пленки имеют ряд преимуществ по сравнению с эпитаксиальными: магнитосопротивление поликристаллических пленок в диапазоне магнитных полей до 35 Т имеет практически линейный характер и не зависит от ориентации пленки в магнитном поле. Делается вывод, что поликристаллические манганитные пленки могут быть использованы при разработке датчиков сильного импульсного магнитного поля. Ил. 8, библ. 5 (на английском языке; рефераты на литовском, английском и русском яз.)