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DEVELOPMENT AND CHARACTERIZATION

OF

THIN-FILM SOLID OXIDE FUEL CELLS

SUBMITTED BY

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1

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Abstract

The emergence of fuel cells (FCs) as important and alternative power generating devices has been accelerated in recent years by the much uplifted environmentalistic concerns and the pessimistic projection of shortage of fossil fuels supply. Among the many types of FC being developed, solid oxide fuel cell (SOFC), which makes use of ionic conducting oxides as electrolytes, has attracted great interest due to its pollutant free operation and high energy conversion efficiency. Currently the size miniaturization and the reduction of operating temperature are the research focuses of SOFC for applications in portable devices. In this connection, the fabrication of ionic conducting oxide thin films and the study of their electrical transport characteristics are necessary.

Basically, solid oxide fuel cell composes of two electrodes (the cathode and anode) separated by a solid electrolyte. For the cathode material, La_{0.85}Sr_{0.15}MnO₃ (LSMO), La_{0.7}Sr_{0.3}MnO₃ and La_{0.7}Sr_{0.3}CoO₃ (LSCO) have been chosen to be used in the present studies as the cathode material because of their good electronic conductivity. The bulk target of the LSMO and LSCO are fabricated by the conventional solid state reaction, and then undergoes high temperature sintering process. LSMO and LSCO are all fabricated in thin film form by pulse laser deposition. The structural properties of the bulk targets and the films are confirmed by x-ray diffractometry.



For the electrolyte material, thin films of $Ce_{0.8}Gd_{0.2}O_{2-\delta}$ (CGO), $Ce_{0.8}Sm_{0.2}O_{2-\delta}$ (CSO) and $La_{1-x}Sr_xGa_{1-y}Mg_yO_{3-\delta}$ (LSGMO) have been fabricated by pulsed laser deposition. We focus our studies on the crystallinity of the as-deposited films and its relationship to the enhanced ionic conductivity.

We started off by studying the effect of processing temperature on the conductivity of the ionic conductors. LSGMO perovskite oxide ion conductor thin films of about 300 nm thick were deposited on a LaAlO₃ (LAO) at *various substrate temperatures* by pulsed laser deposition. Their structural characteristics were studied by x-ray diffractometry. Polycrystalline and epitaxially grown films were revealed for samples grown at different temperatures. Their ionic conductivities were investigated with a two-probe DC technique as a function of temperature over 400 °C – 650 °C range in air. The polycrystalline LSGMO films show a conductivity of 0.19 S/cm while the epitaxial LSGMO films exhibit values of about 0.74 S/cm at 600 °C. This represents a substantial enhancement from the 0.00028 S/cm of the bulk LSGMO measured at the same temperature.

In subsequent studies CSO oxide ion conductor thin films of about 300 nm thick were deposited on a LAO and MgO at the *same substrate temperatures* by pulsed laser deposition. Their structural characteristics were studied by x-ray diffractometry. Due to structural compatibility, polycrystalline and epitaxially grown films were revealed for samples



grown on these two types of substrates. Their ionic conductivities were investigated with a two-probe D.C. and A.C. techniques as a function of temperature over 400 °C – 650 °C range in air. The polycrystalline CSO films grown on MgO show a conductivity of 0.0132 S/cm while the 45 degree twisted epitaxial CSO films grown on LAO exhibit values of about 0.94 S/cm at 600 °C. For the CGO thin films, similar results are

also obtained.

In order to demonstrate the feasibility of applying thin film technology in SOFCs, in particular FC of a single chamber design, we have fabricated patterned bi-layer and tri-layer structure of the LSCO/LSGMO on LAO substrate and Pt/ LSGMO/ LSCO on LAO. Their good structural characteristics have been revealed by XRD and TEM.



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Chapter 1

Introduction

1.1 Introduction

The emergence of fuel cells (FCs) as important and alternative power generating devices has been accelerated in recent years by the much uplifted environmentalistic concerns and the pessimistic projection of shortage of fossil fuels supply. Among the many types of FC being developed, solid oxide fuel cell (SOFC), which makes use of ionic conducting oxides as electrolytes, has attracted great interest due to its pollutant free operation and high energy conversion efficiency. The majority pollutants from SOFC are several orders of magnitude lower than those produced by conventional power generators. NO_x, SO_x and particulates are undetectable for SOFC systems. It directly converts the chemical energy to electrical energy. In comparison, the conventional inductive type of power generators, apart from being dirty pollution emitter, suffer heavy losses from processes involving conversions of fuel to heat, to mechanical energy and then to electrical energy. Currently the size miniaturization and the reduction of operating temperature are the research focuses of SOFC for applications in portable devices [1-2]. In this connection, the fabrication of ionic conducting oxide thin films and the study of their electrical transport characteristics are necessary.



1.2 Working principle of the SOFCs

1.2.1 Mechanism of the SOFCs

Basically, SOFC consists of the two electrodes, called cathode and anode separated by an oxide conducting electrolyte. First of all, the fuel is fed to the anode side to undergo oxidation reaction, followed by releasing electrons to the external circuit. For the cathode side, it provides catalytic reaction sites for the electrochemical reduction of oxidant. For the conventional SOFC, hydrogen and oxygen are chosen as the fuel and oxidant respectively. The oxygen ions transport from cathode to anode through the electrolyte, but it blocks electron transport, forcing the electrons of the reaction to transverse an external load. The schematic diagram of reactions in SOFCs is shown in Fig 1.1 [1].





Fig. 1.1 Working principle of the SOFC

1.2.2 Conduction mechanism in oxides

Ionic conduction takes place with the presence of point defects. Basically, vacant sites should be present to form a continuous path for the ion to jump into and move about. Also, the potential barrier should not be too high for the ion jumping. There are a variety of ways to introduce the vacancies, by doping, by changing of the stoichiometry, or by thermal excitation. By doping is the most common method to generate vacancies for the ionic conducting oxide electrolyte [3]. In this study, the targets of the electrolyte were fabricated by doping as well.



The first solid oxide fuel cell was fabricated in 1937 [4]. Sugiura and his co-worker succeeded in fabricating SOFC in the form of tubular crucible form with ZrO_2 -based ionic conductors as electrolyte, with iron as the anode and Fe_3O_4 as the cathode. They observed a relatively good open-circuit voltages were 1.1 V to 1.2 V at the operating temperature of 1000 °C and 1050 °C respectively. However, it could not be used practically because the current output of the cell was too low.

In the early 1960s, several developments on practical SOFC began. Flat-plate design was chosen as the cell configuration in this period of time. The electrolyte was used in disk form. The drawback of this design is that it required using a very thick electrolyte, thus leading a significant internal resistance loss. Thin-electrolyte concept was then raised.

From 1970 to 1980, various patterns of the SOFC such as segmented cell in series design, sealless tubular design and monolithic design were proposed. At the same time, interest in the flat-plate design has been renewed because of the various new technologies in ceramic fabricating.

Yttria stabilized Zirconia (YSZ) is one of the electrolyte widely used in SOFCs. It possesses adequate oxide ion conductivity and stabilizes in both oxidizing and reducing environment [3,5-6]. This electrolyte, however, requires high operating temperature of up to 1000 °C in order to achieve reasonable ionic conductivity $\sigma_0 \approx 0.1$ S/cm [3,6-7]. Such high operating temperature limits the



choice of usable anode and cathode materials. Cracking and delamination are easily induced during thermal cycling because of the thermal mismatch between the ceramic components. Indeed there are a host of problems associated with the high temperature SOFC operation that one wishes to avoid. Therefore, some research works have been focused on the changing of doping concentration and doping materials to enhance the ionic conductivity during the 1990s [8-12].

However, the enhancement of the ionic conductivity of YSZ through varying the doping concentration and doping material was not enough. As a result, the development of an oxide conductor with higher ionic conductivity is an important subject [13-18].

The high-performance identification of new electrolytes such as La_{0.9}Sr_{0.1}Ga_{0.9}Mg_{0.1}O_{3-δ} (LSGMO) and Ce_{0.8}Gd_{0.2}O_{2-δ} (CGO) represents a major advance towards this end. LSGMO and CGO have ionic conductivity nearly an order of magnitude higher than YSZ and the previous one exhibits almost pure oxide ion conduction in the range of oxygen partial pressures from 10^5 to 10^{-16} Pa [14-15, 19]. For example, the conductivity of CGO is 0.035 S/cm while that of YSZ is less than 0.005 S/cm at 600 °C [16,19-24]. LSGMO exhibits a high oxide ion conductivity of about 0.1 S/cm at the temperature of 800 °C [17-18, 25]. Details of the bulk materials of other doped LaGaO₃ studies are reported elsewhere [13-15, 17-18, 25-34].

The use of thin-film electrolytes is considered a promising technique for SOFC



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miniaturization. Pulsed laser deposition (PLD) is one of the convenient ways to fabricate complex oxide thin films. With the use of properly structural matched substrates epitaxially grown films can be easily obtained. In this study, CGO, CSO and LSGMO thin films have been fabricated on the (100)LaAlO₃ (LAO), (100)MgO and fused silica substrates at different deposition temperature by PLD technique. Randomly oriented polycrystalline and epitaxially grown films were obtained. The DC and AC electrical transport of these films were measured and compared. The bi-layer and tri-layer structure of the SOFC has been fabricated and their structural properties were studied by TEM and XRD as well.



Literature review and basic background theory on SOFC are described in the last few sections in this chapter. A brief introduction of pulsed laser deposition method is presented in Chapter 2. The working mechanism of the pulsed laser deposition as well as the advantages and disadvantages of utilizing pulsed laser deposition to prepare complex oxide thin films are discussed.

Chapter 3 provides the experimental setup of the pulsed laser deposition system. The equipments used in the system are sequentially introduced. Chapter 3 also introduces the various measurement techniques such as XRD, SEM, DC and AC characteristic measurement. The whole deposition process is discussed in detail and epitaxial film grown conditions are emphasized.

In Chapter 4, we focus on the fabrication and characterization of the cathode thin films. The cathode targets have been fabricated using LSCO and different chemical composition of LSMO. The electronic conductivity of the cathode thin films as a function of temperature has been examined, and results of which are presented.

 $Ce_{0.8}Sm_{0.2}O_{2-\delta}$ and $Ce_{0.8}Gd_{0.2}O_{2-\delta}$ ceramic targets used in fabricating the electrolyte thin films are described in Chapter 5. The structural and electrical characteristics of the CGO and CSO thin films have been investigated, and the results of which are furnished in this chapters. In Chapter 6, the investigations are similar to Chapter 5. A different material, LSGMO, however is chosen



instead of CSO and CGO.

Fabrication of tri-layer structure to form a single chamber SOFC is one of the objectives of the present study. So in this research we try to produce the thin film SOFC with good crystallinity. In Chapter 7, structural characterization of the tri-layer thin film has been investigated by XRD and TEM.

The present experimental results and important findings are emphasized and concluded in the last chapter of this thesis. Suggestion for future investigation and development are suggested. The values of this research are fairly evaluated.



Chapter 2

Pulsed laser deposition

2.1 History of pulsed laser deposition

In the mid of 1960s, the ruby laser was used to vaporize and excite atoms from the material surface by Breech and Cross [35]. A few years later, deposition of thin films was obtained by ruby laser. This marked the very beginning of the development of the pulsed laser deposition technique (PLD). With the use of the reliable electronic Q-switches lasers, a very short optical pulse with peak power density exceeding 10^8 W/cm² was available. In subsequent development of the laser technology, high efficiency harmonic generators were developed. They delivered powerful UV radiation. Due to short wavelength of the radiation, enhanced non-thermal interaction at the target surface was achieved. As a result, a quick and efficient congruent evaporation of target materials was made possible. Because of this PLD process was shown to grow stoichiometry thin films easily. For the past thirty years or so, numerous reports have been published for the fabrication of crystalline films grown by PLD [35]. Indeed, epitaxial semiconductor films, heterostructures, and superlattices produced by PLD have all been demonstrated. It has also been shown that the quality of some of the PLD films is comparable to those grown by MBE [36]. However, the most noted success of PLD is on fabrication of stoichiometric complex oxide thin films such as superconducting YBa₂Cu₃O₇ or ferroelectric perovskites.



2.2 Mechanism of pulsed laser deposition

The mechanisms involved in pulsed laser deposition are quite complicated. This is in direct contrast to the simplicity of the set-up itself. In essence high power laser energy is used as an external energy source to vaporize materials that subsequently deposit on substrates to form thin films. Usually a pulsed laser beam is focused onto the surface of a solid target. The strong absorption of the electromagnetic radiation by the solid surface leads to rapid evaporation of the target materials. The evaporated materials, named evaporants, consist of a mixture of energetic species including atoms, molecules, electrons, ions, clusters, micro-sized solid particulates, and molten globules. A glowing plasma plume will be formed from the evaporants immediately in front of the target surface if the ablation is carried out in vacuum. Then the energetic species undergo thermal and non-thermal interaction with the substrate and ultimately lead to film formation and grain growth [37].



2.2.1 The three stages of pulsed laser deposition process

2.2.1.1 Laser-target interaction

When a high power laser beam is focused onto the target, all elements in the target surface are rapidly heated up to their evaporation temperature because of the high energy densities and short pulse duration. Due to the local heating, temperature of the order of 3500 °C is readily reached in a small volume at near the target surface. As a result, materials are dissociated from the target, and then ablated out with stoichiometry as in the target. The ablation mechanisms involve many complex physical phenomena such as collision, thermal and electronic excitation, exfoliation and hydrodynamics [37].

2.2.1.2 Target to substrate gas phase transportation

The ablated materials are highly excited and form a glowing plasma. The plasma plume possesses uniform translational energy of about 10-100eV with small spread. Two types of particles, the thermal induced particle and the non-thermal induced particle will spread out as $\cos\theta$ and $\cos^{n}\theta$, where n>>1 respectively. High ion/neutral ratio and many multiply ionized species are carried in the plasma as well.

2.2.1.3 Nucleation and film growth

The growth of thin films can be categorized into three conventional modes. Three-dimensional island growth (Volmer-Weber) involves the formation of



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isolated islands on the surface. It only occurs when the cohesive energy of the atoms within the film is higher than that of the energy between the films and atoms on the surface. A very smooth epitaxial film is resulted in two-dimensional full-mono-layer growth (Frank-van der Merwe) because of the higher cohesive energy between the films and the surface atoms than that of the film atoms. Mixed growth mode (Stransk-Kastinov) occurs for the interaction strength somewhere in the middle.

2.3 Advantage and disadvantage of pulsed laser deposition

2.3.1 Advantage of pulsed laser deposition

PLD offers several advantages for fabricating films. First of all, the fabricated films normally possess the same stoichiometry as the multicomponent targets. Secondly, The requirement of substrate temperature for fabricating crystalline films by PLD is relatively low compare with those utilizing other deposition method such as thermal evaporation, electron-beam or ion-beam evaporation, d.c. or r.f. magnetron sputtering, chemical vapor deposition (CVD), and molecular beam epitaxy (MBE). Because of the high energy density of the focused laser beam, the as-deposited energetic species have sufficient kinetic energy to migrate to their favorable site. In addition, in-situ growth of different materials is available by the PLD method. For example, using a rotating multi-target holder, the laser beam can be rastered different targets by setting a suitable alignment. As a result, in-situ growth of heterostructures is achieved by this way. The thin film can be deposited in any ambient gas by PLD as well.



Finally, the start-up cost of PLD is low in comparison with, say, molecular beam epitaxy (MBE).

2.3.2 Disadvantage of pulsed laser deposition

There are three main disadvantages of using PLD. The deposition area is very small because of the limited angular spread of the plume. First of all, deposited films of only about 1 cm² can be obtained in a typical PLD geometry. The uniformity of the film thickness cannot be maintained if the area of deposition is too large. The maximum film thickness is obtained at the center of the plasma plume and decreases rapidly with the distance away from the center point [37]. However, the uniformity can be modified by tilting and rotating the substrate. The second undesirable feature of PLD is that the as-deposited films are often covered with large particulates. The formation of the particulates is quite complicated [37]. The particulates size can be as large as $\sim \mu m$, which is bigger than the thickness dimension of the deposited film. As a result, the degradation of the film properties occurs because of the presence of these large particulates on the film. This is particularly damaging in multi-layer systems. However, with the use of the blocking mask placed in between the substrate and the target holder during deposition, the particulates problem could be greatly reduced [38]. Several approaches for reducing the number of particulates such as velocity filter, electromagnetic shutter etc are used as well. The target surface modification represents another disadvantage. Repeated irradiation by high power laser cause pitting on the target surface. If uncheck, these target surface modifications can easily lead to reduced ablation yield and particulates formation.

Chapter 3

Experiments and set-up

3.1 Introduction

All the ionic conducting films were prepared by standard PLD technique using a Lambda Physik KrF eximer laser system (COMPex 2005) with a radiation wavelength of 248 nm. Basically, the PLD experimental setup includes three main parts, namely the laser, the optics system and the vacuum deposition chamber. For the film deposition, it was carried out either under an ambient oxygen at pressure of 100 - 200 mTorr or in vacuum. Prior to load into the chamber for film deposition the substrates were ultrasonically cleaned in acetone followed by thorough rinsing with de-ionized water. The substrates were then secured to a stainless steel resistive heater using silver paste.

In order to investigate the films' quality, scanning electron microscope (SEM) was used to examine the surface morphology of the films. A lot of information could be extracted from the picture of the SEM such as the roughness of the film and the problems associated with particulates. Also, interface quality and the film thickness can be studied directly by inspecting the SEM micrograph of the cross-section of the film/substrate interface. Finally the crystalline quality of the target and the films were characterized by x-ray diffractometry (XRD).

For electrical measurement, the electrical conductivities of all PLD deposited films and the bulk ceramic targets were investigated with a simple two-probe DC technique as a function of temperature from 400 °C to 650 °C in air. The



electrical conductivities, however, may consist of two components, electronic and ionic conductions. For that reason and in order to confirm whether the conductivities are ionic, a two-probe AC measurement was also used.

3.2 Equipment

3.2.1 Excimer Laser

The laser wavelengths used in our PLD system is 248 nm, which lies in the UV range. The interaction between the oxide target and the laser is believed to be dominated by nonthermal interactions rather than by thermal process in this spectral region. As a result, no or very little melting is to take place on the target surface.

Basically, excimer is formed in a gaseous mixture of the component gasses such as Kr, F_2 , He and Ne. The ionic and electronically excited species are created by the avalanche electric discharge excitation (~40 kV). The excited species react chemically to produce the excimer molecules, of which the ground state is repulsive and tends to dissociate rapidly.

In this study, a Lambda Physik COMPex 200 KrF excimer laser was used. The output spatial profile of this particular laser was a "top hat" with a rectangular dimension of $1 \times 3cm^2$. The laser could operate at a maximum repetition rate of 20 Hz. Also, the maximum laser energy per pulse could be reached up to ~ 500 mJ.



One of the advantages offered by PLD technique is flexibility. With the use of the beam steering mirrors, a single laser could serve a number of deposition chambers.

3.2.2 Optics

For coupling of the laser to the target we need to use lenses, apertures, mirrors, and laser window in our deposition system. Instead of ordinary glass optics, uv-grade fused silica lenses and window are necessary because of the required good laser transmittance. UV-grade fused silica can transmit over 90% of the 248 nm radiation from the KrF excimer laser. To achieve the target ablation, laser fluence of several J/cm² is required. The function of the lens is to collect the radiation from the exicmer laser source and concentrate them on to a small spot on the target surface. The length between the target and the lens is about 30 cm, so that the lens with focal length about 30 cm is selected. Therefore, the focused laser spot is converged through the chamber window onto the surface of the target. The dimension of the window is 3 mm thick and 381 mm in diameter.



The schematic diagram of the PLD system is shown in Fig. 3.1. Basically, it consists of a vacuum chamber connecting to a rotary pump, heater/substrate holder, target manipulator, gas flow, and vacuum gauging. The substrate temperature is monitored by a thermocouple embedded in the heater face plate.



Fig. 3.1 The schematic diagram of the PLD deposition system

All the ionic conducting oxide thin films produced in this research were deposited in a chamber which was evacuated by a rotary pump to vacuum of no better than 10^{-3} Torr. Oxygen environment was needed for growing oxygen stoichiometric thin films. As a result, a gas inlet port was used for afflux of oxygen gas of 99.7% purity into the chamber to a desired film growth oxygen pressure of, say, ~100mTorr.



However, for some cases such as growing of TiN films, the growth may require a high vacuum condition. So, an additional diffusion pump was used to evacuate the experimental chamber to a base pressure of about 10^{-6} Torr.

3.3 Testing instrument

3.3.1 X-ray diffraction

The crystal structure of thin films are characterized by an x-ray diffractometer (Philip mode X'pert system) operated in four-circle mode. Fig. 3.2 shows a schematic diagram of the x-ray diffraction of a crystal. X-rays have high energies and short wavelength. When it falls on the atoms of a crystal, a portion of the beam will be scattered in all directions by the atoms in accordance to their arrangement. Since crystalline solid consists of a regular array of atoms and it leads to a natural three-dimensional "diffraction grating" for x-rays. By analyzing the scattered radiation distribution the crystalline structure of the material can therefore be deduced.

When a parallel monochromatic beam of x-rays is incident on the film, absorption and reflection from the crystal planes will occur. The atoms in the crystal become diffraction centers. As a result, constructive interference in certain direction will be produced.


Fig. 3.2 Constructive interference of a lattice structure



If the diffraction satisfies the Bragg's Law, the reflected beam will possess maximum intensity.

 $n\lambda = 2d_{hkl}\sin\theta$.

where (λ) , (d_{hkl}) and (θ) stands for x-rays wavelength, inter-atomic spacing and angle of the diffracted beam respectively.

The d_{hkl} value in cubic structure is calculated as

$$d_{hkl} = \frac{a_0}{\left(h^2 + k^2 + l^2\right)^{1/2}}$$

where h, k, and l are the Miller index and a_0 is the lattice constant. Table 3.1 lists the d_{hkl} values in different crystal structure



Table 3.1	Equation	of interplanar	spacing of	of different	materials	structure
			~			

System	Interplanar Spacing
Cubic	$d_{hkl} = \frac{a_0}{(h^2 + k^2 + l^2)^{\frac{1}{2}}}$
Tetragonal	$\frac{1}{d_{hkl}} = \frac{h^2 + k^2}{a^2} + \frac{l^2}{c^2}$
Hexagonal	$\frac{1}{d_{hkl}} = \frac{4}{3} \left(\frac{h^2 + hk + k^2}{a^2} \right) + \frac{l^2}{c^2}$
Rhombohedral	$\frac{1}{d_{hkl}} = \frac{(h^2 + k^2 + l^2)\sin^2 \alpha + 2(hk + kl + hl)(\cos^2 \alpha - \cos \alpha)}{a^2(1 - 3\cos^2 \alpha + 2\cos^3 \alpha)}$
Orthorhombic	$\frac{1}{d_{hkl}^2} = \frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2}$
Monoclinic	$\frac{1}{d_{hkl}^2} = \frac{1}{\sin^2 \beta} \left(\frac{h^2}{a^2} + \frac{k^2 \sin^2 \beta}{b^2} + \frac{l^2}{c^2} - \frac{2hl \cos \beta}{ac} \right)$
Triclinic	$\frac{1}{d_{hkl}^2} = \frac{a^2 b^2 c^2}{V^2} \begin{bmatrix} \frac{h^2 \sin^2 \alpha}{a^2} + \frac{k^2 \sin^2 \beta}{b^2} + \frac{l^2 \sin^2 \gamma}{c^2} + \frac{2hk}{ab} (\cos \alpha \cos \beta - \cos \gamma) + \frac{2kl}{bc} (\cos \beta \cos \gamma - \cos \alpha) \\ + \frac{2lh}{ac} (\cos \gamma \cos \alpha - \cos \beta) \end{bmatrix}$



3.3.2 Scanning electron microscopy

Scanning electron microscopy (SEM) is a high-resolution imaging technique. In this project we will use SEM to investigate the surface morphology and cross-section of the deposited films.

The working principle of SEM is that a high energy and tightly focused electron beam is scanned across the specimen surface. The electrons can undergo several interactions with the specimen. The interactions can be classified into two types, elastic and inelastic events. As a result, a variety of signals such as secondary electrons, backscattered electrons and x-ray are generated. Each of them can be used to characterize a material with respect to specific properties. It is because the collected signals vary with the changes in composition, texture or topography at the specimen surface.

Not all the specimen can be analyzed by SEM directly. For example, analyzing non-conducting materials is difficult. A negative charge will build up gradually from bombardment by the high energy electron beam if the specimen is non-conducting. Thus, an abnormal contrast and splitting of the image result from the uneven distribution of the negative charge on the sample. To avoid this charge accumulation, a very thin (10-20 nm thick) coating of gold layer is normally placed on the surface of the sample.

3.4 Experimental procedures

3.4.1 Target fabrication

All the pulsed laser ablation targets were fabricated by the standard solid state reaction method. The required amount of constituent oxide powder was weighed according to the desired stoichiometric ratio. The powder was mixed with ethanol and then ball milled for 9 hours. In order to get rid of the organic components from the mixed powder and to allow the chemical reaction to occur, calcinations was carried out. The calcinated product was then re-ground again into powder in mortar. This calcinated powder was compressed by an oil-compressor at a pressure of 4.5 Ton into about 3 mm thick circular pellets. Each of the calcinations and sintering processes were done in air and lasted for 10 hours at the desired temperature. Finally, XRD and Energy Dispersive X-ray (EDX) were carried out to investigate the structural properties and the chemical composition of these ceramic targets, respectively.

3.4.2 Substrate preparation

In this study, fused silica, single crystal LaAlO₃ (LAO) and MgO were selected to be the substrates for film growth. All the substrates were purchased from commercial vendors, with the same dimension of 0.5mm (T) x 5mm (W) x 10mm (L). In order to remove the grease due to the contamination on the surface, which will greatly affect the quality of the as-prepared film, the substrate must be thoroughly cleaned before it can be used. We cleansed and



degreased the substrates ultrasonically for 10 minutes using spectroscopic

grade acetone.

3.4.2 Deposition process

Before the start of the deposition, proper alignment of the target, substrate and optics was made. The target was mounted on a rotating target holder as shown in Fig. 3.1. The target-substrate distance was kept at 45 mm. In order to reduce particulates, a shadow mask was placed in between the substrate and the target. Before the actual ablation process the mirrors and the lens were firstly and finely aligned, so that the laser beam passed the window of the chamber and focused onto the target surface. The chamber was then continuously evacuated by a rotary pump until the pressure was below 10mTorr. After that, oxygen was filled into the chamber to the desired deposition pressure, such as 100mTorr. A final check of the beam alignment was achieved by observing the laser induced plasma plume. Two important points should be carefully attended to. The first is that the plume should emanate from the target at a direction normal to the target surface, while the other is that the tip of the plume should point toward the centre of the substrate holder.

After these delicate alignment processes had been carefully completed, the chamber was re-filled back to atmospheric pressure. The substrate was secured to a stainless steel resistive heater/substrate holder using silver paste. The reason for the choice of silver paste in the adhesion is that it can act as the heat conduction medium in between the substrate and the heater. In order to find out



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the thickness of the film, a small strip of stainless steel was placed at a corner of the substrate surface. As a result, the thickness of the film could be determined by surface profiler (Tencor P-10 surface profiler). Then the chamber was evacuated by the rotary pump to 10 mTorr again. The ohmic heater was turned on and waited until reaching the desired deposition temperature. Then, oxygen was filled into the chamber to 100 mTorr. When all the parameters for film deposition were stable, the laser was pulsed at a repetition rate of 10 Hz with an on-target laser fluence of $3J/cm^2$. The deposition time was lasted for 10 minutes to obtain films of ~300 nm thick. Finally, post annealing was carried out at the same deposition temperature for 10 minutes, so that better crystalline films were achieved.

Several approaches for reducing the number of particulates such as velocity filter, electromagnetic shutter etc are used as well.



3.5 Structural analysis of thin films

3.5.1 Thickness measurement

To check the thickness of our PLD thin films, a Tencor P-10 surface profiler was used. A schematic diagram of an alpha step machine is shown in Fig. 3.3. The step of the film is produced by partly masking with the stainless steel strip during deposition process. The needle probe with a tip diameter of $10\mu m$ is scanned across the step, so that the difference in height between the film and substrate would be measured and the film thickness would be deduced.

Because of the non-uniformity of the film, SEM image of cross-section of the film is often employed to counter check the thickness measurement.



Fig 3.3 Film thickness measurement by surface profiler

1

3.5.2 In-plane and out-of-plane structure measurement

The structure of the thin films was characterized by x-ray diffractometer (XRD). Fig 3.4 shows the three axes rotation of the sample. In order to investigate the epitaxial quality of the deposited thin films, θ -2 θ scan, ω scan, 360° - ϕ scan were carried out. The polycrystalline phases of the film and the crystalline orientation quality of the films were determined by θ -2 θ scan and ω scan respectively. The 360° - ϕ scan was used to determine the in-plane mosaicity and the epitaxial growth relationship of the film and substrate. The CuK_{α} radiation (1.54Å) was used for the XRD and the unwanted CuK_{β} radiation was filtered out by a nickel filter.



Fig. 3.4 Experimental geometry, showing four primary axes of goniometer, x-ray tube, detector and slits



Out-of-plane lattice parameter of the film can be determined from the θ -2 θ profile. The various crystalline phases and orientation of the film are revealed. Only one set of planes of a family (h00) should be observed if epitaxial films are grown. Nonetheless, we cannot guarantee that the films are epitaxially grown on the substrate even if one set of planes from a single family of peaks. We can only conclude that he films are highly oriented in this direction.

To perform the ω scan (rocking curve), the 20 value is fixed at a selected diffraction peak and the angle θ is scanned (rocked) for a few degrees. The value of the Full Width at Half Maximum (FWHM) of such a ω scan reflects the degree of the crystalline grain orientation in the thin films. The smaller the value of FWHM, the better is the grain orientation. Generally, if it is $\leq 1^{\circ}$, a highly oriented film is suggested.

In fact, θ -2 θ scan and rocking curve analyses only give out-of-plane information and are not adequate to infer the epitaxial relationship of the film and the substrate. In order to characterize the in-plane structure of the film, ϕ -scan is needed. First of all, the ϕ angle is tilted to 45° for cubic structures, the 2 θ and θ angles are locked onto the diffraction peaks of a selected plane such as (100). As a result, the original plane (100) is changed to (101). From the 360° ϕ -scan profile, four peaks with separation of 90° corresponding to (101), ($\overline{1}0\overline{1}$), ($10\overline{1}$), and ($\overline{1}01$) should be observed for a highly oriented films. If the ϕ angles of the four peaks of the film and those of the substrate are perfectly matched, it can be said that the film is cube-on-cube epitaxially grown on the substrate.

3.6 Electrical analysis of thin films

3.6.1 Resistivity against temperature relation by DC measurement

A simple Resistance-Temperature (R-T) measuring setup as shown schematically in Fig. 3.5 was used. The present investigation mainly concerns the electrical transport properties of electrolyte at reduced operating temperature. Due to the relatively large resistance of the electrolyte thin film(~several M Ω), a two-point contact setup was sufficient to provide accurate measurement. As shown in Fig. 3.5, two Pt electrodes with equal dimension are coated by PLD with well defined separation. The electrical conductivities were investigated as a function of temperature from 723K to 923K in air. For all our electrolyte samples conductivity at below 700K was too low to be of any significance.



Fig. 3.5 Schematic set-up of DC two-probe method

3.6.2 Resistivity against temperature relation by AC measurement

The contribution of electronic conductivity, however, cannot be eliminated under the present DC measurement. For this reason a two-probe AC method was employed for yielding the ionic contribution from the mixed electrical conductivity. The experimental set-up of the AC two-probe method is shown in fig. 3.6. The impedance spectrum was obtained by a computer controlled impedance analyzer over the frequency range of 100 Hz – 1 MHz at temperature from 400 °C to 650 °C. Our low frequency end measurement limited to 100 Hz is set by our present available impedance analyzer. The amplitude of the applied voltage in the AC impendence measurement is usually less than 100 mV. However, in measuring our samples the signal to-noise ratio is too small. The large noise background is probable due to EMI pick up by the external circuit. Proper shielding of the external wiring is inhibited due to the fact that our samples need to be placed inside a high temperature oven for temperature dependence measurement. With these considerations, an applied voltage of 500 mV was chosen.



Fig. 3.6 Schematic set-up of AC two-probe method

3.6.3 Theory of AC measurement

The application of the AC measurement is to resolve the resistance of grain boundaries, grain interiors and the electrode. Fig. 3.7 shows the impedance spectrum and the equivalent circuit of the polycrystalline YSZ. Two arcs should be observed in the impedance spectrum, the left one being due to the grain lattice (bulk) and the other one to the grain boundaries. Because of the ionic conduction, it exhibits a capacitance effect in the equivalent circuit [39].





Fig. 3.7 The impedance spectrum and the equivalent circuit of the polycrystalline YSZ

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In some case, only one semicircle is observed. It represents that the ionic conductivity of the grain boundaries is relatively high. As a result, the grain boundaries form "short circuit" and the grain boundary impedance was eliminated effectively. This phenomenon always appears in thin film ionic conducting electrolyte. There are two possible ways that could result in one arc. The first scenario is that the grain size is comparable to the thickness of the film, so that the overall impedance from grain lattice and grain boundary results in one arc represented by parallel equivalent circuit. The other scenario is that the grain lattice arc is too small to be detectable, so that the measured arc is from grain boundaries [40].



Fig. 3.8 The impedance spectrum of thin film YSZ



Chapter 4

Fabrication and characterization of $La_{0.7}Sr_{0.3}MnO_{3,}$ $La_{0.85}Sr_{0.15}MnO_3$ and $La_{0.7}Sr_{0.3}CoO_3$ cathode materials

4.1 Introduction

A prime function of the cathode in SOFC is to provide reaction sites for the electrochemical reduction of the oxidant. The basic requirement for cathode should be good stability in oxidizing environment at room temperature, operating temperature and fabrication temperature, so that there is no phase transformation. Also, the electronic conductivity must be sufficiently high to minimize ohmic losses and having enough catalytic activity for the oxidant gas reaction at the operating temperature. In order to avoid second phase formation, chemical reaction and elemental interdiffusion between the cathode and electrolyte should be limited. Because of the high temperature operation (600 °C) in SOFC, cracking is easily occurred. The thermal expansion between the cathode and the electrolyte should be similar as well [1, 41].

La_{1-x}Sr_xMnO₃ (LSMO) has been widely used as cathode material in SOFC. The reasons are that it is low cost, possesses of sufficient electronic conductivity in the oxidizing environment and is not easy to have chemical interaction with the conventional electrolyte. Its thermal expansion coefficient is ~ 12.5 X 10^{-6} K⁻¹, showing a slight dependence on the composition of the target [1]. For the conventional electrolyte materials such as LSGMO, CGO and CSO, the thermal



expansion coefficient are ~ $12 \times 10^{-6} \text{ K}^{-1}$, $11.5 \times 10^{-6} \text{ K}^{-1}$ and $11.9 \times 10^{-6} \text{ K}^{-1}$ respectively [1, 33, 42]. The excellent thermal expansion coefficient matching between LSMO and electrolyte materials are ideal for producing crack-free thin film interface.

La_{1-x}Sr_xCoO₃ (LSCO) has similar properties to that of LSMO. The thermal expansion is ~ 26.2 X 10^{-6} K⁻¹ at temperature above 700 °C. This is too high compared with that of the electrolyte materials [43]. Also, LSCO may react with the electrolyte materials at 1000 °C to form secondary phase at the interface [1]. This unwanted interface layer affects the conductivity of the electrolyte so much. However, if the operating temperature is below 600 °C, the thermal expansion is significantly reduced to 17.7 X 10^{-6} K⁻¹ [43]. As a result, LSCO is possible for the used as cathode material in thin film form, not only stable in oxidizing environment, but also having higher electronic conductivity than LSMO.

In this study, one LSCO target and two LSMO targets of different composition $(La_{0.85}Sr_{0.15}MnO_3 \text{ and } La_{0.7}Sr_{0.3}MnO_3)$ have been prepared. The electronic conductivities as a function of temperature of the LSMO and LSCO films were investigated. The structural characteristics of the films and targets were evaluated by x-ray diffraction and SEM.



4.2 Structural characteristics of $La_{0.7}Sr_{0.3}CoO_3$, La_{0.85}Sr_{0.15}MnO₃ and La_{0.7}Sr_{0.3}MnO₃ targets

4.2.1 Fabrication of $La_{0.7}Sr_{0.3}CoO_3$, $La_{0.85}Sr_{0.15}MnO_3$ and $La_{0.7}Sr_{0.3}MnO_3$ targets

LSMO and LSCO targets were fabricated by the standard solid states reaction method. The chemicals involved and their appropriate weight ratios are shown in Table 4.1.

Table 4.1 Required chemical and their weight

	La_2O_3	SrCO ₃	MnO ₂	Co_3O_4
$La_{0.7}Sr_{0.3}CoO_3$				
Molar Weight	325.809 g	147.63 g	-	240.797 g
Desired Weight	11.76 g	4.56 g	-	8.27 g
La _{0.7} Sr _{0.3} MnO ₃				
Molar Weight	325.809 g	147.63 g	86.95 g	-
Desired Weight	11.76 g	4.56 g	8.96 g	-
La _{0.85} Sr _{0.15} MnO ₃				
Molar Weight	114.16 g	114.16 g	86.95 g	-
Desired Weight	14.27 g	2.28 g	8.96 g	-

According to the desired stoichiometric ratio, the required amount of oxide powder was weighed. The powder was mixed with ethanol and then ball milled for 9 hours. In order to get rid of the organic components from the mixed powder and to allow the chemical reaction to occur, calcinations was carried out. The calcinated powder was compressed by an oil-compressor at a pressure of 4.5 Ton into about 3 mm thick circular pellets. Sintering was then carried out



to form the desired target. The calcinations and sintering processes were tabulated in table 4.2. Each of the calcinations and sintering processes were done in air and lasted for 10 hours at the desired temperature.

	Calcination temperature	Sintering temperature
La _{0.7} Sr _{0.3} CoO ₃	1100 °C	1400 °C
La _{0.7} Sr _{0.3} MnO ₃	1100 °C	1350 °C
La _{0.85} Sr _{0.15} MnO ₃	1100 °C	1350°C

 Table 4.2 Calcination and sintering temperature

4.2.2 Structural characteristics of $La_{0.7}Sr_{0.3}CoO_3$, $La_{0.85}Sr_{0.15}MnO_3$ and $La_{0.7}Sr_{0.3}MnO_3$ targets

To investigate the structural characteristics of the as prepared targets, XRD was performed. Fig. 4.1 and Fig. 4.2 are the θ -2 θ scans of the LSMO (La_{0.85}Sr_{0.15}MnO₃ and La_{0.85}Sr_{0.15}MnO₃) and La_{0.7}Sr_{0.3}CoO₃ targets respectively. The major x-ray diffraction peaks are in good match with those listed on the database (International centre for the Diffraction Data, ICDD). In order to verify the exact chemical composition, EDX analysis was carried out.





Fig. 4.1 XRD patterns of LSMO target with different composition (a) $La_{0.7}Sr_{0.3}MnO_3$ and (b) $La_{0.85}Sr_{0.15}MnO_3$





Fig. 4.2 XRD patterns of La_{0.7}Sr_{0.3}CoO₃ target



4.3 Structural characteristics of $La_{0.7}Sr_{0.3}CoO_3$, $La_{0.7}Sr_{0.3}MnO_3$ and $La_{0.85}Sr_{0.15}MnO_3$ thin films

4.3.1 Fabrication of LSMO and LSCO thin films

All the LSMO and LSCO films were deposited by PLD. These materials have lattice constant of around 3.9 Å. In order to achieve a lattice matching condition for epitaxial growth, commercial single crystal (100) LaAlO₃ (LAO) (a = 3.8 Å) and (100)MgO (a = 4.2 Å) were chosen as the substrates. Basically, both of the LAO and MgO are cubic structure. All films were deposited at a substrate temperature of 650 °C and an ambient oxygen pressure of 100mtorr. The laser fluence was kept to ~ 5 Jcm⁻². The deposition time of LSMO and LSCO thin films were last for 10 minutes. The thickness of the resulted films was about 300 nm. Two parallel platinum (Pt) strips were deposited on the top of the films acting as the electrodes for electrical measurement. A sufficiently high substrate temperature could improve the adhesion and create a good ohmic contact between the oxide films and the Pt electrode. Therefore, the deposition of Pt was carried out at a substrate temperature of 300 °C and at a pressure of several mtorr.

4.3.2 Structural characterization of the LSMO film

The structural properties of a single layer of LSMO film grown on (100) LAO substrate was examined. LSMO has a peusdocubic structure. The out-of-plane lattice constant **a** was found to be \sim 3.9 Å. This is very close to that of LAO and epitaxial growth of LSMO on LAO is expected. We have also used MgO single



crystal as substrate in order to eliminate the possible electronic conduction effect that occurs at high temperatures on using LAO substrate [6].

The lattice dimension of LSMO is composition dependant - a smaller lattice constant **a** for more strontium doping. For example, the lattice constants of La_{0.85}Sr_{0.15}MnO₃ is 3.88 Å while that of La_{0.7}Sr_{0.3}MnO₃ is 3.87 Å. Fig. 4.3 and Fig. 4.4 present the θ -2 θ scans of LSMO thin film grown on (100) LAO and (100) MgO single crystals respectively. The θ -2 θ scans confirm the growth of single phase LSMO film on LAO and MgO. Only (h00) oriented peaks are observed. The FWHM of La_{0.7}Sr_{0.3}MnO₃/LAO and La_{0.85}Sr_{0.15}MnO₃/LAO is 0.29° and 1.05° respectively. They are shown in Fig. 4.5. Fig. 4.6 shows the rocking curves of LSMO/MgO structure. The FWHM of rocking curves of the LSMO/MgO structures is greater than those of LSMO/LAO structures. It suggests that the crystalline quality of LSMO films grown on LAO is better. This is not totally unexpected. The lattice constant of MgO is 4.2 Å, which is substantially bigger than that of LSMO. This large lattice mismatch inevitably degraded the epitaxial film quality.

So far the out-of-plane structural characteristic of the LSMO film was determined. However the in-plane structural quality and grain mosaicity could not be determined by the above measurement. Therefore, additional ϕ scan was applied to examine the in-plane parameter of the films. Fig. 4.7 and 4.8 show the ϕ scan of (202) LSMO reflection peaks. For this ϕ scan, the angle of χ was tiled 45°, so that (h01) phase family aligned normal to the incident x-ray beam at some specific ϕ angles. For example, in a cubic system the (h01) family planes meet the incident x-ray beam at Bragg's condition four times during a



 360° ϕ -rotation. Consequently four distinguish peaks separated by 90° are obtained in the ϕ -scan. The four fold symmetry observed in the XRD patterns confirms the cubic structure of the LSMO/LAO substrate as well as LSMO/MgO. The four characteristic peaks of the LSMO reflections are very sharp and their ϕ angle values match with those of the LAO and MgO reflections. This is a clear indication of cube-on-cube epitaxially grown LSMO films on LAO and MgO substrates.

In conclusion, single phase (100) LSMO was grown on both of the single crystal (100) LAO and MgO substrate epitaxially. Good crystalline structure and grain orientation were found for the LSMO film deposited at substrate temperature of 650 °C on LAO. The crystallinity is slightly poorer for the LSMO film grown on MgO substrate.





Fig. 4.3 X-ray θ -2 θ diffraction patterns for (a)La_{0.7}Sr_{0.3}MnO₃/LAO structure and (b) the La_{0.85}Sr_{0.15}MnO₃/LAO structure





Fig. 4.4 X-ray θ -2 θ diffraction patterns for (a)La_{0.7}Sr_{0.3}MnO₃/MgO structure and (b) the La_{0.85}Sr_{0.15}MnO₃/MgO structure





Fig. 4.5 The rocking curve of the (a) $La_{0.7}Sr_{0.3}MnO_3/LAO$ and (b) $La_{0.85}Sr_{0.15}MnO_3/LAO$





Fig. 4.6 The rocking curves of (a) $La_{0.7}Sr_{0.3}MnO_3/MgO$ and (b) $La_{0.85}Sr_{0.15}MnO_3/MgO$





Fig. 4.7 ϕ scans of (a)(i) (202) La_{0.7}Sr_{0.3}MnO₃ and (ii) (202) LAO reflection and (b)(i) (202) La_{0.85}Sr_{0.15}MnO₃ and (ii) (202) LAO reflection peaks





Fig. 4.8 ϕ scans of (a)(i) (202) La_{0.7}Sr_{0.3}MnO₃ and (ii) (202) MgO reflection and (b)(i) (202) La_{0.85}Sr_{0.15}MnO₃ and (ii) (202) MgO reflection peaks



4.3.3 Structural characterization of the LSCO film

Fig. 4.9 presents the x-ray diffraction profiles of LSCO films grown on the (100) LAO and (100) MgO. Single phase crystalline films grown on these two different substrates were confirmed. The FWHM of rocking curves of LSCO/LAO is smaller than those of LSCO/MgO. Their corresponding values are displayed in Fig. 4.10. In ϕ scan analysis, the four characteristic reflection peaks of LSMO, LAO and MgO are observed as shown in Fig. 4.11 and Fig 4.12. The films ϕ -scan peaks are sharp and at the same angle values as that of the substrates. As argued before, cube-on-cube epitaxially grown LSCO film on LAO and MgO substrate are evident.





Fig. 4.9 X-ray θ -2 θ diffraction patterns of La_{0.7}Sr_{0.3}CoO₃ grown on (a) LAO and (b) MgO





Fig. 4.10 The rocking curve of the (a) $La_{0.7}Sr_{0.3}CoO_3/LAO$ and (b) $La_{0.7}Sr_{0.3}CoO_3/MgO$





Fig. 4.11 $\,\phi$ scans of (a) (202) $La_{0.7}Sr_{0.3}CoO_3$ and (b) (202) LAO reflection peaks





Fig. 4.12 φ scans of (a) (202) $La_{0.7}Sr_{0.3}CoO_3$ and (b) (202) MgO reflection peaks



4.4 Electrical Characterization of $La_{0.7}Sr_{0.3}CoO_3$, La_{0.7}Sr_{0.3}MnO₃ and La_{0.85}Sr_{0.15}MnO₃ thin films

4.4.1 Electrical properties of the LSCO and LSMO films

For being a premier cathode for SOFC, materials need to have thermal stability, matching expansion coefficient, and good electronic conductivity. The thermal properties of LSCO and LSMO have been studied and reported elsewhere [1, 41]. The consensus is that both of the materials are suitable for use as cathode in SOFC. In fact, both LSMO and LSCO are known to be good electronic conducting oxides. Typically, the requirement for the electronic conductivity is greater than 50 S/cm at 1000 °C for bulk material [41]. A simple two point probe was used to study the electronic conductivity of the LSMO and LSCO films with different substrates as a function of temperature range from 400 °C-650 °C. Although a four-point probe technique is more accurate to determine the films conductivity, the present set up is nevertheless adequate to provide inductive measurements. Fig. 4.13 shows the electronic conductivity of the films as a function of temperature. At 600 °C, the La_{0.7}Sr_{0.3}CoO₃/LAO film exhibits an electronic conductivity of 3360 S/cm, while that of the La_{0.7}Sr_{0.3}MnO₃/LAO is only 200 S/cm. As a result, LSCO thin film is an excellent choice for the cathode in SOFC. The enhanced conductivity of LSCO grown on LAO is probably due to improved film crystallinity as suggested by fig. 4.10(a).





Fig. 4.13 The electrical conductivity of the cathode thin films as a function of temperature


Chapter 5

Fabrication and characterization of $Ce_{0.8}Gd_{0.2}O_{2-\delta}$ and $Ce_{0.8}Sm_{0.2}O_{2-\delta}$ electrolyte materials

5.1 Introduction

In SOFC, the electrolyte serves to conduct oxygen ions between the cathode and the anode. In other word, excess ions produced at one electrode due to catalytic chemical reaction are transported via the electrolyte to the other electrode and created a potential difference. Thus electrons flowing round an external circuit linking the electrodes thus balance potential difference. As a result, a closed loop electrical circuit is complete in the SOFC. Basically, the electrolyte should have similar thermal expansion and chemically compatible with the two electrode materials. Cracking and other unwanted phase formation should be by all means avoided. However, when it comes to the crunch, it is the high ionic conductivity that remains the most important aspect of electrolytes.

In this study, $Ce_{0.8}Sm_{0.2}O_{2-\delta}(CSO)$ and $Ce_{0.8}Gd_{0.2}O_{2-\delta}(CGO)$ laser ablation ceramic targets have been prepared. Electrolyte thin films made out of these targets have been fabricated on the (100)LaAlO₃ (LAO), MgO and fused silica substrates at different deposition temperature by PLD technique. The structural characteristics of the films and targets were revealed by x-ray diffraction and SEM. In the present studies randomly oriented polycrystalline and epitaxially grown films have been obtained. The DC and AC electrical transport of these electrolyte films were measured and compared.



5.2 Structural characteristics of $Ce_{0.8}Sm_{0.2}O_{2-\delta}$ and $Ce_{0.8}Gd_{0.2}O_{2-\delta}$ targets

5.2.1 Fabrication of the $Ce_{0.8}Sm_{0.2}O_{2-\delta}$ and $Ce_{0.8}Gd_{0.2}O_{2-\delta}$ targets

All the $Ce_{0.8}Sm_{0.2}O_{2-\delta}$ and $Ce_{0.8}Gd_{0.2}O_{2-\delta}$ targets were fabricated by standard solid state reaction method. The chemicals involved and their appropriate weight ratios are shown in Table 5.1.

Table 5.1 Required chemical and their weight

	CeO ₂	Sm_2O_3	Gd_2O_3
$Ce_{0.8}Gd_{0.2}O_{2\text{-}\delta}$			
Molar Weight	172.115 g	-	362.498 g
Desired Weight	14.2 g	-	3.73 g
$Ce_{0.8}Sm_{0.2}O_{2-\delta}$			
Molar Weight	172.115 g	348.715 g	-
Desired Weight	14.2 g	3.6 g	-

The amount of oxide powder was weighed according to the desired stoichiometric ratio. The powder was mixed with ethanol and then ball milled for 9 hours. Calcinations was carried out in order to get rid of the organic components from the mixed powder and to allow the chemical reaction to occur. The calcinated powder was compressed by an oil-compressor at a pressure of 4.5 Ton into 3 mm thick circular pellets. Sintering was then carried out to form the desired target. The calcinations and sintering processes were tabulated in table 5.2. Each of the calcinations and sintering processes were done in air and



lasted for 10 hours at the desired temperature.

	Calcination temp	Sintering temp
$Ce_{0.8}Sm_{0.2}O_{2-\delta}$		
	1150 °C	1450 °C
$Ce_{0.8}Gd_{0.2}O_{2\text{-}\delta}$		
	1150 °C	1450 °C

Table 5.2	Calcination	and sintering	e temperature
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5.2.2 Structural characteristics of $Ce_{0.8}Sm_{0.2}O_{2-\delta}$ and $Ce_{0.8}Gd_{0.2}O_{2-\delta}$ targets

XRD was carried out for structural characterization of the as-prepared targets. Fig. 5.1 is the θ -2 θ scans of the Ce_{0.8}Sm_{0.2}O_{2- δ} and Ce_{0.8}Gd_{0.2}O_{2- δ} targets. According to the database (International centre for the Diffraction Data, ICDD), the major x-ray diffraction peaks show good matching. EDX was carried out to verify the chemical composition.





Fig. 5.1 XRD patterns of the (a) CSO target and (b) CGO target

5.3 Structural characteristics of $Ce_{0.8}Sm_{0.2}O_{2-\delta}$ and $Ce_{0.8}Gd_{0.2}O_{2-\delta}$ thin films

5.3.1 Fabrication of $Ce_{0.8}Sm_{0.2}O_{2-\delta}$ and $Ce_{0.8}Gd_{0.2}O_{2-\delta}$ thin films

All the $Ce_{0.8}Sm_{0.2}O_{2-\delta}$ and $Ce_{0.8}Gd_{0.2}O_{2-\delta}$ thin films were deposited by PLD. For these materials, their lattice constant are more or less the same at around 5.4 Å. In order to investigate their ionic conductivity with different crystallinity structure, different substrate and deposition temperature were used to fabricate the films. To facilitate a lattice matching condition, commercial single crystals of (100) LaAlO3 (LAO) and (100) MgO were chosen as the deposition substrate. LAO and MgO are both cubic in structure and has a lattice constant about 3.9 Å and 4.2 Å respectively. Fused silica was used as substrate as well in order to fabricate amorphorous/polycrystalline films. All films were fabricated at different substrate temperature but under the same ambient oxygen pressure of 100mtorr. The laser fluence was kept to ~ 5 Jcm^{-2} . The PLD duration for growing thin films of CGO and CSO was 10 minutes. The thickness of the as-deposited films is ~ 400 nm. Two parallel Pt strips were deposited on the top of the films. A sufficiently high substrate temperature could improve the adhesion and create good ohmic contact between the oxide films and the Pt electrode. Therefore, Pt was deposited at a substrate temperature of 300 °C and at a pressure of several mtorr. Fig. 5.2 shows the SEM cross-sectional image of the CGO/LAO heterostructures deposited at 650 °C. The actual thicknesses of the CGO and CSO films are easily obtained from the SEM cross-section picture.





Fig. 5.2 The SEM cross-sectional image of 400 nm CGO/LAO film deposited at 650 °C



Single layer CGO films grown on (100) LAO, (100) MgO and fused silica substrates were examined. Special attention was directed towards the structural properties of films grown on LAO and MgO substrates. CGO has a cubic structure and the out-of-plane lattice parameter \mathbf{a} was found to be ~5.4 Å. Although CGO has a large lattice mismatch with LAO and MgO, a 45 degree twisted epitaxial growth on LAO because the diagonal of the LAO crystal is matched with the side of CGO crystal. For the CGO growth on MgO, cube-on-cube epitaxial growth on MgO is expected due to the domain matching.

Fig. 5.3 shows the θ -2 θ scans of a CGO thin film grown on (100) LAO single crystal with different deposition temperature. Films grown at 300 °C show no diffraction peaks, suggesting an amorphous nature. Films deposited on LAO at 650 °C exhibit strong diffraction peaks. However only the (h00) oriented peaks are observed. This is a clear indication that we have single phase crystalline films here. The XRD rocking curve on the CGO (200) reflection are depicted in Fig. 5.4. The full width at half maximum (FWHM) of the curve is ~0.93°.

So far the out-of-plane structural characteristic of the CGO films was determined. Additional ϕ scan was applied to examine the in-plane parameter of the films. The procedure for performing the 360^{0} - ϕ scan on CGO films is similar to that described in Chapter 4 for LSMO films. Fig. 5.5 shows the ϕ scan of (202) CGO reflection peaks. The four characteristic peaks of the CGO reflections are very sharp and distinct. Their ϕ angle values differ from that of



the corresponding LAO reflections by 45° . This is a clear indication of a 45° twisted epitaxial growth of CGO film on LAO substrate.

Typical θ -2 θ x-ray diffraction patterns of the CGO thin films grown on MgO substrate at different substrate temperatures are shown in Fig. 5.6. Fig. 5.6(a) confirms the growth of single phase CGO film on MgO at 650 °C. Again only the (h00) oriented peaks are observed. The rocking curve of the (200) reflections from CGO films as shown in Fig. 5.7 reveal a FWHM of ~2.35°. This suggests a rather poor crystalline quality. Fig. 5.8 shows the ϕ scan of (202) CGO reflection peaks. The four fold symmetry observed in the XRD ϕ -scan confirms the cubic structure of the grown CGO films. The four characteristic peaks of the CGO reflections, though weak, are clearly discernable and aligned perfectly with those of the MgO. This is an unmistakable sign of a cube-on-cube epitaxially grown CGO film on MgO substrate. θ -2 θ scan of CGO thin film grown on fused silica is shown in Fig. 5.9. A few weak diffraction peaks are seen. They correspond to reflections from (200), (311) and (400) planes. It therefore can be concluded that the CGO film deposited on fused silica is of randomly oriented polycrystalline structure.

In conclusion, well crystallized CGO films are obtained at growth temperature of 650 °C. Randomly oriented polycrystalline films are found to grow on fused silica (amorphous) substrates. Single phase (100) CGO films, however, are seen to grow on lattice matched single crystal (100) LAO and (100) MgO substrates via a 45° twisted epitaxy and a cube-on-cube expitaxy respectively.





Fig. 5.3 X-ray θ -2 θ diffraction patterns for CGO films grown on LAO at substrate temperature (a) 650 °C and (b) 300 °C



Fig. 5.4 Rocking curve of (200) CGO film on LAO grown at 650 °C



Fig. 5.5 ϕ -scan of (a) (202) CGO and (b) LAO





Fig. 5.6 X-ray θ -2 θ diffraction patterns for CGO films grown on MgO at substrate temperature (a) 650 °C and (b) 300 °C



Fig. 5.7 Rocking curve of (200) CGO film on MgO grown at 650 °C



Fig. 5.8 ¢-scan of (a) (202) CGO and (b) (202) MgO





Fig. 5.9 X-ray θ-2θ diffraction patterns for CGO films grown on fused silica at 650 °C

5.3.3 Structural characterization of the $Ce_{0.8}Sm_{0.2}O_{2-\delta}$ film

Similar to CGO described in last section (5.3.2), single-layer CSO thin films were grown on (100) LAO, (100) MgO and fused silica substrates at different substrate temperature. Fig. 5.10 displays the x-ray θ -2 θ scans of the CSO/LAO heterostructures prepared at substrate temperatures of 300 °C and 650 °C. Once again films deposited at 300 °C are amorphous. Well crystalline films are obtained for deposition carried out at 650 °C. For these crystalline films only reflections from the (h00) family planes are observed, implying the single phased CSO film growth. The FWHMs of the rocking curves of the films are less than 1° as illustrated in Fig. 5.11. The ϕ -scan profile of the (202) CSO and



the corresponding profile of the LAO substrate are represented in Fig. 5.12. As revealed in a similar manner as for CGO, CSO films grown on LAO also shows a 45° twisted epitaxy.

Fig. 5.13, Fig. 5.14 and Fig. 5.15 are the x-ray diffraction results for CSO films deposited on MgO substrates. As before, we can concluded that (100) CSO films can be cube-on-cube heteroepitaxially grown on (100) MgO.

For CSO thin films grown on fused silica, Fig. 5.16 shows a typical x-ray θ -2 θ scans profile. It reveals similar result with that of the CGO/fused silica films.





Fig. 5.10 X-ray θ -2 θ diffraction patterns for CSO films grown on LAO at substrate temperature (a) 650 °C and (b) 300 °C





Fig. 5.11 Rocking curve of (200)CSO film on LAO grown at 650 $^{\circ}\mathrm{C}$





Fig. 5.12 ¢-scan of (a) (202) LAO and (b) (202) CSO





Fig. 5.13 X-ray θ-2θ diffraction patterns for CSO films grown on MgO at substrate temperature (a) 650 °C, (b) 550 °C and (c) 300 °C





Fig. 5.14 Rocking curve of (200) CSO film on MgO grown at 650 $^{\circ}\mathrm{C}$





Fig. 5.15 ϕ -scan of (a) (202) CSO and (b) (202) MgO





Fig. 5.16 X-ray $\theta\text{-}2\theta$ diffraction patterns for CSO films grown on fused silica at 650 $^{\circ}\text{C}$



5.4 Electrical properties of the $Ce_{0.8}Gd_{0.2}O_{2-\delta}$ and $Ce_{0.8}Sm_{0.2}O_{2-\delta}$ thin films

CGO and CSO are known to be good ionic conducting oxides. Both the CGO and CSO films in this study have been fabricated from their corresponding bulk ceramic targets of the desired compositions. Their ionic conductivities were investigated with a two-probe DC and AC techniques as a function of temperature from 400 $^{\circ}$ C to 650 $^{\circ}$ C in air.

5.4.1 Electrical properties of the $Ce_{0.8}Gd_{0.2}O_{2-\delta}$ and $Ce_{0.8}Sm_{0.2}O_{2-\delta}$ thin films

5.4.1.1 DC Measurement of $Ce_{0.8}Gd_{0.2}O_{2-\delta}$ and $Ce_{0.8}Sm_{0.2}O_{2-\delta}$ thin films

CGO and CSO targets were fabricated by the technique as mentioned in section 5.2.1. Thin films of these materials were coated on different substrates and at different substrate temperatures by PLD method. Their electrical properties were measured by a two-probe DC technique as a function of temperature from 400 °C to 650 °C. Fig. 5.17 shows the electrical conductivity of the CSO and CGO films fabricated with different processing parameters. At a measuring temperature of 600 °C, an electrical conductivity of 0.94 S/cm was obtained for the epitaxial CSO film grown on LAO, while the amorphous CSO film grown on the same substrate at 300 °C shows only a modest value of 0.2 S/cm. For the CSO films and CGO films grown on MgO, the electrical conductivity tends to increase with the film growth temperature. Similar trend occurs on CSO film



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and CGO film grown on fused silica. It is evident that the better is the crystallinity, the higher is the electrical conductivity. For the bulk CGO target, its electrical conductivity is two orders of magnitude lower than that of the films grown on MgO substrate. As a result, thin films of CGO and CSO shows a significant enhancement in electrical conductivity as compared with their bulk materials.

Ionic conductivity is known to depend on the size of cation dopant. The radii of Sm^{3+} and Gd^{3+} are 0.1 nm and 0.097 nm respectively. In order to investigate empirically the size effect on the ionic conductivity, we have compared the electrical conductivity between samples of CSO and CGO in table 5.3. Apparently CSO shows better conductance. It is generally known that the ionic radius of Sm^{3+} is similar to that of Ce^{4+} . The lattice has therefore less strain and fewer association of the cation with oxygen ion vacancy. This induces greater mobility for oxygen ions, thus higher ionic conductivity. To confirm whether the electrical conductivity is primarily from ionic contribution, AC measurement of conductivity has been used.

THE HONG KONG POLYTECHNIC UNIVERSITY 香港理工大學 (a) MgO (300 °C) Log electrical conductivity (S/cm) 0 MgO (550 °C) ☆ MgO (650 °C) ۸ LAO (650 °C) -1 LAO (300 °C) FS (610 °C) Bulk CSO Δ ٥ -2 ☆ ۵ ជ ۸ ☆ -3 \triangle ☆ \triangle \bigtriangleup -4 Δ \triangle \triangle -5 \bigtriangleup -6 1.4 1.2 1.3 1.0 1.1 1.5 1.6 1000/Temperature (K⁻¹) 0 LAO (650 °C) Log electrical conductivity (S/cm) LAO (650 °C) LAO (300 °C) MgO (650 °C) MgO (300 °C) (b) ۸ • -1 fused silica (650 °C) Bulk CGO Δ -2 ٥ ٥ ð -3 \triangle \triangle -4 \triangle \triangle \triangle -5 \triangle -6 1.1 1.2 1.3 1.4 1.0 1.5 1.6

Fig. 5.17 The electrical conductivity of (a) CSO thin films and (b) CGO thin films as a function of 1000/Temperature

1000/Temperature (K⁻¹)



Table 5.3Comparison of the electrical conductivity between CGO and CSO
thin films at 600 °C

		Electrical conductivity (600 °C) (S/cm)	
Substrate	Substrate	$Ce_{0.8}Gd_{0.2}O_{2-\delta}$	$Ce_{0.8}Sm_{0.2}O_{2-\delta}$
	temperature (°C)		
LAO	650	0.375	0.94
	300	0.36	0.2
MgO	650	0.0124	0.0132
	300	0.0016	0.0039
Fused silica	650	0.0105	0.0147
Bulk Sample	-	0.00015	0.00033

5.4.1.2 AC Measurement of $Ce_{0.8}Gd_{0.2}O_{2-\delta}$ and $Ce_{0.8}Sm_{0.2}O_{2-\delta}$ thin films

The impedance spectra of a CSO thin film grown on LAO at 650 °C and at 300 °C are shown in fig. 5.18 (a) and fig. 5.18(b) respectively. The temperature range of the present measurement is 400 °C to 650 °C. As expected, only one semicircle is produced. It may originate from the bulk or from the grain boundary resistance [40]. As the temperature is increased, a conspicuous shrinkage of the semicircle is observed. The ionic conductivity can be derived from the intercept at the Z_{real} axis. The semicircle, however, disappears when the temperature is raised up to 500 °C. The likely reason for this observation is that there is significant electronic conduction. Indeed, at high temperatures such as 500 °C or above, LAO can no longer remain a good insulator. CGO/LAO films exhibit similar result.



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Fig. 5.19 shows the impedance spectra of CSO thin films grown on MgO at different substrate temperatures. Again the measuring temperature ranges from 400 °C to 650 °C. The spectra of CGO/MgO heterstructure are presented in Fig. 5.20. This time the semicircle can be clearly observed even at high measuring temperatures. It is because the MgO substrate can retain its nonconductive nature in the temperature range of the present studies. For the same measuring temperature, the diameter of the semicircle in the spectra is smaller (higher ionic conductivity) for films grown at higher temperature than for films grown at lower temperature. This agrees well with the XRD studies that better crystallinity films generate higher ionic conductivity.

For the CSO and CGO films grown on fused silica, an easily recognizable semicircle in the spectra is observed. This is due to the nonconductive feature of fused silica. As a result, it possesses similar ionic conductivity with that of CSO/MgO and CGO/MgO films at a substrate temperature of 650 °C. The details are shown in Fig. 5.21 and Fig. 5.22 respectively.

Because of the electronic contribution from the LAO substrate at high temperature, and in order to make comparison between the ionic conductivity of epitaxial film and polycrystalline film, comparison were made at the measuring temperatures 400 °C and 450 °C. From figure 5.22 and 5.23, one can conclude that the resistance of epitaxial films is a factor of four smaller to that of the polycrystalline film. In conclusion, epitaxial CGO and CSO films should exhibit bigger ionic conductivity enhancement.













Fig. 5.18(a) The impedance spectra of a CSO thin film grown on LAO at 650 °C as a function of temperature from 400 °C to 650 °C







Fig. 5.18(b) The impedance spectra of a CSO thin film grown on LAO at 300 °C as a function of temperature from 400 °C to 650 °C



Fig. 5.19 The impedance spectra of CSO thin films grown on MgO at (a) 650 °C (b) 550 °C and (c) 300 °C as a function of temperature from 400 °C to 650 °C





Fig. 5.20 The impedance spectra of CGO thin films grown on MgO at (a) 650 °C and (b) 300 °C as a function of temperature



Fig. 5.21 The impedence spectra of CSO thin film grown on fused silica at 650 °C as a function of temperature from 400 °C to 650 °C



Fig. 5.22 The impedance spectra of a CGO thin film grown on fused silica at 650 °C as a function of temperature from 450 °C to 650 °C





Fig. 5.23(a) The impendance spectra of CSO thin films grown on LAO at 650 °C and MgO at 650 °C at measuring temperature 450 °C



Fig. 5.23(b) The impedance spectra of CSO thin films grown on LAO at 650 °C and MgO at 650 °C at measuring temperature 400 °C





Fig. 5.24 The impedance spectra of CGO thin films grown on LAO at 650 °C and MgO at 650 °C at measuring temperature 450 °C



Chapter 6

Fabricationandcharacterizationof $La_{1-x}Sr_xGa_{1-y}Mg_yO_{3-\delta}$ electrolyte materials

6.1 Introduction

The strontium doped LaGaMgO₃ (LSGMO) perovskite with a superior oxide ion conductivity of approximately 0.1 S/cm at 800 °C is a promising electrolyte for low temperature SOFCs [13, 17, 18, 30, 32, 34, 43]. Compared with CGO and CSO, it has negligible electronic conductivity below 1000 °C over a wide range of oxygen partial pressures ($P_{O2} = 1$ atm. to 10^{-22} atm.) [13-15, 32, 43]. Similar thermal expansion coefficient with that of YSZ, LSMO and LSCO has been reported [33]. As a result, LSMO and LSCO cathodes are eminently suitable matches with LSGMO electrolyte. However, due to the relatively high cost of gallium oxide, LSGMO has suffered to be the electrolyte in conventional SOFCs [17, 44]. With the use of modern thin-film fabrication technology, the development of a miniaturized SOFC is possible. In the practical point of view, the ionic conduction efficiency at low temperature operation rather than the cost of the electrolyte is the major concern. In this respect, LSGMO may have an important role to play in future low temperature thin film SOFCs.

In this study, three different composition LSGMO ($La_{0.9}Sr_{0.1}Ga_{0.9}Mg_{0.1}O_{3-\delta}$, $La_{0.8}Sr_{0.2}Ga_{0.8}Mg_{0.2}O_{3-\delta}$ and $La_{0.8}Sr_{0.2}Ga_{0.85}Mg_{0.15}O_{3-\delta}$) targets have been prepared. Based on these ceramic targets LSGMO thin films of about 450 nm


thick have been fabricated on the (100) LAO, (100)MgO and fused silica substrates at different deposition temperatures by PLD technique. The structural characteristics of the films and targets have been evaluated by x-ray diffraction and SEM. Both randomly oriented polycrystalline and epitaxially grown films are obtained. The DC and AC electrical transport properties of these electrolyte films are measured and compared.

6.2 Structural characteristics of $La_{1-x}Sr_xGa_{1-y}Mg_yO_{3-\delta}$ targets

6.2.1 Fabrication of the La_{1-x}Sr_xGa_{1-y}Mg_yO_{3-δ} targets

All the $La_{1-x}Sr_xGa_{1-y}Mg_yO_{3-\delta}$ targets were fabricated by the standard solid state reaction method. The chemicals involved and their appropriate weight ratios are listed in Table 6.1.

	La ₂ O ₃	SrCO ₃	Ga ₂ O ₃	MgO
$La_{0.9}Sr_{0.1}Ga_{0.9}Mg_{0.1}O_{3-\delta}$				
Molar Weight	325.809 g	147.63 g	187.44 g	40.304 g
Desired Weight	15.11 g	1.52 g	8.69 g	0.41 g
$La_{0.8}Sr_{0.2}Ga_{0.8}Mg_{0.2}O_{3-\delta}$				
Molar Weight	325.809 g	147.63 g	187.44 g	40.304 g
Desired Weight	13.43 g	3.04 g	7.73 g	0.83 g
$La_{0.8}Sr_{0.2}Ga_{0.85}Mg_{0.15}O_{3-\delta}$				
Molar Weight	325.809 g	147.63 g	187.44 g	40.304 g
Desired Weight	13.43 g	3.04 g	8.21 g	0.62 g

Table 6.1 Required chemicals and their weight



The preparation procedure for LSGMO was essentially the same as for CGO and CSO described in 5.2.1. The calcinations and sintering temperatures are tabulated in table 6.2. Each of the calcinations and sintering processes were done in air and lasted for 10 hours at the desired temperatures.

 $\begin{tabular}{|c|c|c|c|c|} \hline Calcination temp & Sintering temp \\ \hline La_{0.9}Sr_{0.1}Ga_{0.9}Mg_{0.1}O_{3-\delta} & & & \\ \hline 1100\ ^{\circ}C & 1450\ ^{\circ}C \\ \hline La_{0.8}Sr_{0.2}Ga_{0.8}Mg_{0.2}O_{3-\delta} & & & \\ \hline 1100\ ^{\circ}C & 1450\ ^{\circ}C \\ \hline La_{0.8}Sr_{0.2}Ga_{0.85}Mg_{0.15}O_{3-\delta} & & \\ \hline 1100\ ^{\circ}C & 1450\ ^{\circ}C \\ \hline \end{array}$

Table 6.2 Calcination and sintering temperature

6.2.2 Structural characteristics of theLa_{1-x}Sr_xGa_{1-y}Mg_yO_{3- δ} targets

XRD was carried out for structural characterization of the as-prepared targets. Fig. 6.1 depicts the XRD θ -2 θ scans of the La_{0.9}Sr_{0.1}Ga_{0.9}Mg_{0.1}O_{3- δ}, La_{0.8}Sr_{0.2}Ga_{0.8}Mg_{0.2}O_{3- δ} and La_{0.8}Sr_{0.2}Ga_{0.85}Mg_{0.15}O_{3- δ} targets. Diffraction peaks are in good agreement with those listed in ICDD. EDX analysis of the targets reveals the actual chemical compositions to be the same as the designed values.







6.3 Structural characterization of $La_{1-x}Sr_xGa_{1-y}Mg_yO_{3-\delta}$ thin films

6.3.1 Fabrication of $La_{1-x}Sr_xGa_{1-y}Mg_yO_{3-\delta}$ thin films

All the LSGMO films were prepared by the usual PLD technique using our existing setup. LSGMO has a lattice constant of around 3.9 Å. This is almost the same as that of pseudocubic LAO. We have therefore used LAO as the substrates to grow epitaxial LSGMO thin films. We have also used fused silica and (100)MgO to fabricate amorphous and polycrystalline films. Apart from using different substrates and different substrate temperatures, all other deposition parameters were kept the same. For examples, the laser fluence was ~ 5 Jcm^{-2} , the ambient oxygen pressure was 100 mtorr and the deposition duration was 10 minutes. The thickness of the films was measured by alpha-step profiler and by close examination of the scanning electron micrographs of the x-section of the films. Fig. 6.2 shows a typical SEM cross-section image of the La_{0.8}Sr_{0.2}Ga_{0.8}Mg_{0.2}O₃₋₆/LAO heterostructure grown at 730 °C. All LSGMO films show fairly uniform thickness of about 450 nm. Parallel strips of Pt electrodes were deposited on the top of the films for electrical characterizations.



 $\begin{array}{ccccc} Fig. & 6.2 & The & SEM & cross-sectional & image & of & 450 & nm \\ & & La_{0.8}Sr_{0.2}Ga_{0.8}Mg_{0.2}O_{3-\delta}/LAO & film & deposited & at 730 \ ^{\circ}C \end{array}$



6.3.2 Structural characterization of the $La_{1-x}Sr_xGa_{1-y}Mg_yO_{3-\delta}$ films

Single-layer LSGMO films grown on (100) LAO, (100) MgO and fused silica substrates were examined. The structural properties of the films grown on LAO substrates, in particular, were studied in details. LSGMO has a primitive cubic perovskite structure with a lattice parameter $\mathbf{a} = 3.911$ Å. As the LSGMO exhibit similar lattice constant with LAO, heteroepitaxial growth of LSGMO is expected.

The XRD θ -2 θ scans of La_{0.9}Sr_{0.1}Ga_{0.9}Mg_{0.1}O_{3- δ}, La_{0.8}Sr_{0.2}Ga_{0.8}Mg_{0.2}O_{3- δ} and La_{0.8}Sr_{0.2}Ga_{0.85}Mg_{0.15}O_{3- δ} thin films grown on (100) LAO single crystal with different deposition temperature are presented in Fig. 6.3, Fig 6.4 and Fig 6.5 respectively. Based on these θ -2 θ scans, it is apparent that good crystalline LSGMO films were grown on LAO at 730 °C. Strong reflections from LSGMO (*l*00) family planes are clearly seen. Diffraction from other family planes is not discernable. Weak peaks due to Cu K_{β} radiation are also indexed. The XRD rocking curves of the (200) reflections from different composition of LSGMO are shown in Fig. 6.6. All crystalline films show FWHM of below 1°. No LSGMO diffraction peaks have been observed for films deposited at substrate temperature below 500 °C.

Additional XRD ϕ -scan analysis was used to examine the in-plane structural quality of the films. Fig. 6.7, Fig 6.8 and Fig 6.9 show the 360^{0} - ϕ scans of (202) reflections of La_{0.9}Sr_{0.1}Ga_{0.9}Mg_{0.1}O_{3- δ}, La_{0.8}Sr_{0.2}Ga_{0.8}Mg_{0.2}O_{3- δ} and La_{0.8}Sr_{0.2}Ga_{0.85}Mg_{0.15}O_{3- δ} respectively. Four sharp peaks separated by 90° are



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obtained in the ϕ -scans. The four fold symmetry observed in the XRD patterns confirms the cubic structure of the as grown LSGMO and LAO substrate. The four characteristic peaks of the LSGMO reflections are very sharp and their ϕ angles are perfectly aligned with those of the LAO substrate. It infers LSGMO films were cube-on-cube epitaxially grown on LAO.

In order to compare the ionic conductivity of the LSGMO with different crystalline quality, we have deposited LSGMO films on MgO substrates. Fig. 6.10 shows the θ -2 θ x-ray diffraction patterns of the three different compositions LSGMO thin films grown on MgO at substrate temperature of 730 °C. Only peaks of MgO were observed. This suggests that the LSGMO films are either amorphous or randomly oriented polycrystalline. Fig. 6.11 shows the La_{0.8}Sr_{0.2}Ga_{0.8}Mg_{0.2}O_{3- δ} grown on fused silica at 730°C. Only the Pt peaks is seen in the XRD profile.

In conclusion, good crystalline structure and grain orientation were found for LSGMO films deposited at substrate temperature of 730 °C. Hetroepitaxial growth of (100)LSGMO on single crystal (100)LAO is also obtained. For LSGMO films grown on MgO and fused silica, they are either amorphous or polycrystalline of randomly oriented crystal grains.





Fig. 6.3 X-ray θ -2 θ diffraction patterns for La_{0.9}Sr_{0.1}Ga_{0.9}Mg_{0.1}O_{3- δ} films grown on LAO at substrate temperature (a) 730 °C and (b) 500 °C





Fig. 6.4 X-ray θ -2 θ diffraction patterns for $La_{0.8}Sr_{0.2}Ga_{0.8}Mg_{0.2}O_{3-\delta}$ films grown on LAO at substrate temperature (a) 730 °C and (b) 500 °C





Fig. 6.5 X-ray θ -2 θ diffraction patterns for La_{0.8}Sr_{0.2}Ga_{0.85}Mg_{0.15}O_{3- δ} film grown on LAO at substrate temperature (a) 730 °C and (b) 500 °C







Fig. 6.7 ϕ -scan of (a) (202) $La_{0.9}Sr_{0.1}Ga_{0.9}Mg_{0.1}O_{3\text{-}\delta}$ and (b) LAO





Fig. 6.8 ϕ -scan of (a) (202) $La_{0.8}Sr_{0.2}Ga_{0.8}Mg_{0.2}O_{3\text{-}\delta}$ and (b) LAO





Fig. 6.9 $\phi\text{-scan}$ of (a) (202) $La_{0.8}Sr_{0.2}Ga_{0.85}Mg_{0.15}O_{3\text{-}\delta}$ and (b) LAO

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Fig. 6.10 X-ray θ -2 θ diffraction patterns for (a) $La_{0.9}Sr_{0.1}Ga_{0.9}Mg_{0.1}O_{3-\delta_{1}}$ (b) $La_{0.8}Sr_{0.2}Ga_{0.8}Mg_{0.2}O_{3-\delta}$ and (c) $La_{0.8}Sr_{0.2}Ga_{0.85}Mg_{0.15}O_{3-\delta}$ film grown on MgO at substrate temperature 730 °C





Fig. 6.11 X-ray θ -2 θ diffraction patterns for $La_{0.8}Sr_{0.2}Ga_{0.8}Mg_{0.2}O_{3-\delta}$ film grown on fused silica at substrate temperature 730 °C



6.4 Electrical properties of the $La_{1-x}Sr_xGa_{1-y}Mg_yO_{3-\delta}$ thin films

LSGMO is known to be ionic conducting oxides. In this study all the LSGMO films with different composition have been fabricated from their corresponding bulk ceramic targets of the desired compositions. Their ionic conductivities as oxide electrolyte thin films were investigated with two-probe DC and AC techniques over a temperature range from 400 °C to 650 °C in air.

6.4.1 Electrical properties of the $La_{1-x}Sr_xGa_{1-y}Mg_yO_{3-\delta}$ thin films

6.4.1.1 DC Measurement of La_{1-x}Sr_xGa_{1-y}Mg_yO_{3-δ} thin films

All LSGMO targets were fabricated as mention in section 6.2.1. Their corresponding thin films were fabricated on different substrates and at different deposition temperatures by PLD. Fig. 6.12 shows the electrical DC conductivities of various LSGMO films plotted against the measuring temperature. Table 6.3 compares the electrical conductivity between $La_{0.9}Sr_{0.1}Ga_{0.9}Mg_{0.1}O_{3-\delta}$, $La_{0.8}Sr_{0.2}Ga_{0.8}Mg_{0.2}O_{3-\delta}$ and $La_{0.8}Sr_{0.2}Ga_{0.85}Mg_{0.15}O_{3-\delta}$ thin films. At 600 °C, an electrical conductivity of 0.74 S/cm was achieved for the $La_{0.8}Sr_{0.2}Ga_{0.8}Mg_{0.2}O_{3-\delta}$ film grown on LAO at substrate temperature of 730 °C, while that of the film grown on the same substrate at 500 °C is only 0.19 S/cm. For the LSGMO films grown on MgO and fused silica, all of them exhibit conductivities of about 10⁻³ S/cm. It is worth to note that this figure is significantly smaller than that of the films grown on LAO. Apparently epitaxial LSGMO films exhibit much enhanced ionic conductivity. It agrees with the



results of measuring CGO and CSO films performed in Chapter 5. In order to confirm whether the electrical conductivity is originated from ionic contribution, AC measurement has been conducted as well.





Table 6.3 Comparison of the electrical conductivity between $La_{0.9}Sr_{0.1}Ga_{0.9}Mg_{0.1}O_{3-\delta}$, $La_{0.8}Sr_{0.2}Ga_{0.8}Mg_{0.2}O_{3-\delta}$ and $La_{0.8}Sr_{0.2}Ga_{0.85}Mg_{0.15}O_{3-\delta}$ thin films at 600 °C

		Electrical conductivity (600 °C) (S/cm)			
Substrate	Substrate temperature (°C)	La _{0.9} Sr _{0.1} Ga _{0.9} Mg _{0.1} O _{3-δ}	$La_{0.8}Sr_{0.2}Ga_{0.8}Mg_{0.2}O_{3\text{-}\delta}$	$La_{0.8}Sr_{0.2}Ga_{0.85}Mg_{0.15}O_{3-\delta}$	
LAO	730	0.59	0.74	0.52	
	500	0.098	0.19	0.22	
MgO	730	1.7 X 10 ⁻³	7.1 X 10 ⁻³	4.6 X 10 ⁻³	
Fused silica	730	-	1.5 X 10 ⁻³	-	

6.4.1.2 AC Measurement of La_{1-x}Sr_xGa_{1-y}Mg_yO_{3-δ} thin films

The impedance spectra of $La_{0.8}Sr_{0.2}Ga_{0.8}Mg_{0.2}O_{3-\delta}$ thin films grown on LAO at 730 °C and at 500 °C are shown in fig. 6.13 (a) and fig. 6.13(b) respectively. As expected, only one semicircle is produced. This can either come from the bulk boundary resistance or from the grain boundary resistance [39-40]. As the temperature is increased, the semicircle shrinks in size. The ionic conductivity can be derived from the intercept at the Z_{real} axis. The semicircle disappears when the temperature is raised up to 500 °C. The likely reason is that there is a significant electronic conduction from the LAO substrate. LSGMO films with different composition exhibit similar spectra.



Fig. 6.14 shows the impedance spectra of $La_{0.8}Sr_{0.2}Ga_{0.8}Mg_{0.2}O_{3-\delta}$ thin film grown on MgO at 730 °C. The semicircle remains distinct even at high measuring temperatures of up to 650 °C. This is the result of the nonconductive nature of MgO substrate.

A well defined semicircle is shown in Fig. 6.15 for the $La_{0.8}Sr_{0.2}Ga_{0.8}Mg_{0.2}O_{3-\delta}$ film grown on fused silica too. It possesses similar ionic conductivity to that of LSGMO/MgO film grown at substrate temperature of 730 °C.

In conclusion, LSGMO films exhibit an enhancement in ionic conductivity over their bulk counterpart. Our results also clearly demonstrate that the epitaxial films exhibit better ionic conduction than the amorphous/polycrystalline films. However, the choice of substrate should be nonconductive in order to eliminate contribution from unwanted electronic conduction.











Fig. 6.13(a) The impedance spectra of $La_{0.8}Sr_{0.2}Ga_{0.8}Mg_{0.2}O_{3-\delta}$ thin film grown on LAO at 730 °C as a function of temperature from 400 °C to 650 °C









Fig. 6.13(b) The impedance spectra of $La_{0.8}Sr_{0.2}Ga_{0.8}Mg_{0.2}O_{3-\delta}$ thin film grown on LAO at 500 °C as a function of temperature from 450 °C to 650 °C





Fig. 6.14 The impedance spectra of $La_{0.8}Sr_{0.2}Ga_{0.8}Mg_{0.2}O_{3-\delta}$ thin film grown on MgO at 730 °C as a function of temperature from 500 °C to 650 °C



Fig. 6.15 The impedance spectra of $La_{0.8}Sr_{0.2}Ga_{0.8}Mg_{0.2}O_{3-\delta}$ thin film grown on fused silica at 730 °C as a function of temperature from 500 °C to 650 °C



Chapter 7

Fabrication and characterization of patterned bi-layer and tri-layer SOFC

7.1 Introduction

In order to demonstrate the feasibility of applying thin film technology in SOFC, in particular FC of a single chamber design, we have fabricated patterned bilayer and trilayer heterostructures. Our results as reported in the previous chapters have \demonstrated the fact that the electrical conductivity increases with the crystalline quality of the oxide films. LSCO exhibits the best electronic conductivity among the others. As a result, it was selected as the cathode for our heterostructures. Because of the similarity in the lattice constant between LSCO and LSGMO, epitaxial LSGMO directly grown on LSCO is expected. In the present work we have grown LSCO/LSGMO and Pt/LSGMO/LSCO on LAO substrates. Their excellent structural characteristics have been revealed by XRD and TEM.



7.2 Fabrication and structural characterization of bi-layer and tri-layer thin films

7.2.1 Fabrication of $La_{0.7}Sr_{0.3}CoO_3/$ $La_{0.8}Sr_{0.2}Ga_{0.8}Mg_{0.2}O_{3-\delta}/$ LAO thin film

The heterostructure of the La_{0.7}Sr_{0.3}CoO₃/La_{0.8}Sr_{0.2}Ga_{0.8}Mg_{0.2}O₃₋₈/LAO was fabricated by PLD method. LSGMO acted as the electrolyte, was deposited under 100 mTorr of oxygen and at a deposition temperature of 730 °C. For the fabrication of the top LSCO electrode, the deposition temperature and the ambient oxygen pressure were kept at 650 °C and 100 mTorr, respectively. The PLD duration for depositing both the LSCO and LSGMO thin films was 10 minutes each.

7.2.2 Structural characterization of the $La_{0.7}Sr_{0.3}CoO_3/La_{0.8}Sr_{0.2}Ga_{0.8}Mg_{0.2}O_{3-\delta}/LAO$ thin films

7.2.2.1 Structural characterization of by XRD

The lattice constant of the LSCO and LSGMO are more or less the same at about 3.9 Å. The XRD θ -2 θ scans of the LSCO/LSGMO/LAO heterostructure are presented in Fig. 7.1. Apart from reflections from the LAO substrate, only one sharp peak was recorded. Although two distinct peaks from the LSCO and LSGMO (*l*00) family planes should appear. The observed single peak may originate from the overlapping of the LSCO and LSGMO reflections.





Fig. 7.1 X-ray θ -2 θ diffraction patterns for LSCO/LSGMO/LAO heterostructure film



7.2.3 Fabrication of Pt/ $La_{0.8}Sr_{0.2}Ga_{0.8}Mg_{0.2}O_{3-8}/La_{0.7}Sr_{0.3}CoO_3/$ LAO thin films

The trilayer heterostructure of Pt/La_{0.8}Sr_{0.2}Ga_{0.8}Mg_{0.2}O₃₋₈/La_{0.7}Sr_{0.3}CoO₃/LAO was also fabricated by PLD method. The bottom LSCO electrode was deposited at 650 °C and under 100 mTorr ambient oxygen pressure. LSGMO acting as the electrolyte in between the LSCO and Pt, was deposited under ambient oxygen of 100 mTorr and at a substrate temperature of 730 °C. The deposition time for growing the LSCO and LSGMO thin films was 10 minutes and 20 minutes, respectively. Platinum (Pt), playing the role of anode, was deposited at a substrate temperature of 300 °C and at a higher vacuum of several mTorr.



7.2.4 Structural characterization of the Pt/La_{0.8}Sr_{0.2}Ga_{0.8}Mg_{0.2}O₃₋₈/ La_{0.7}Sr_{0.3}CoO₃/ LAO thin film

7.2.4.1 Structural characterization of by XRD

The XRD θ -2 θ scans of Pt/LSGMO/LSCO/LAO heterostructure are presented in Fig. 7.2. Aside from the peaks of the reflection from the (100)LAO substrate, relatively low intensity of the LSCO and LSGMO peaks are detected. This implies that the as-deposited heterostructure has poor structural quality.



Fig. 7.2 X-ray θ -2 θ diffraction patterns for Pt/LSGMO/LSCO/LAO heterostructure film



7.2.4.2 Structural characterization of by transmission electron microscopy

Because of there are no peaks observed in XRD analysis, we have utilized transmission electron microscopy (TEM) to make further investigations. The bright field image of the LSGMO/ LSCO/ LAO is obtained and shown in Fig. 7.3. A clear sharp interface can be identified. The thickness of the LSCO and LSGMO are seen to be 450 nm and 700 nm respectively. Fig. 7.4 shows the electron diffraction pattern of LAO, LSCO and LSGMO respectively. By measuring the patterns, LAO is found to belong to cubic lattice with (110) orientation. If there is epitaxial growth of the LSCO and LSGMO on LAO substrate, the patterns of the two layers will be in the (110) orientation as well. However, the diffraction patterns of LSCO and LSGMO are quite complicated. From the diffraction pattern, LSCO exhibits highly oriented structure, while a diffuse ring and some lattice pattern are observed in LSGMO, indicated that the LSGMO is in polycrystalline structure. Another diffraction pattern from the cross-section of the film is shown in Fig. 7.5. A clear LAO(110) diffraction pattern is identified. However, there is a bright spot labeled g1. In order to investigate the g1 spot, dark-field imaging was carried out. Fig. 7.6 shows the dark-field image of the g1 spot. From the dark-field image, two grains are observed. The upper and the lower represent the LSGMO and LSCO grains respectively. Both of the two grains exhibit the same orientation. As a result, there remains good potential to fabricate epitaxial LSGMO/LSCO/LAO heterostructure if one can locate the proper deposition condition.



Fig. 7.3 The bright field image of the LSGMO/ LSCO/ LAO heterostructure





Fig. 7.4 The electron diffraction pattern of (a) LAO, (b) LSCO and (c) LSGMO





Fig. 7.5 Another diffraction pattern from the cross-section of the film



Fig. 7.6 The dark-field image of the g1 spot



Chapter 8

Conclusion and future work

All oxide cathode and electrolyte thin films used in this study for SOFC have been fabricated by PLD method on different substrate materials. The ablation targets were made by conventional solid state reaction of constituent oxides according to the desired stoichiometic ratios. Thickness of the films was measured by a Tencor P-10 surface profiler and from SEM cross-section images. The crystallinity of the thin films was studied by XRD, SEM and TEM. The electrical properties such as DC conduction and AC conduction were also measured. The relations between the structural and electrical properties of the films were investigated. In addition Bi-layer and tri-layer structures were fabricated and their structural properties were characterized.

In the present work we have fabricated electrical conducting La_{0.7}Sr_{0.3}CoO₃, La_{0.7}Sr_{0.3}MnO₃ and La_{0.85}Sr_{0.15}MnO₃ thin films on LAO and MgO single crystal substrates by PLD. All the films are epitaxially grown at 650 °C. However, the FWHM of rocking curve is narrower for films deposited on LAO, suggesting that the crystallinity of the film on LAO is better. The best electrical conductivity is obtained in the heteroepitaxial LSCO/LAO sample. A high electronic conductivity of 3360 S/cm at 600 °C is measured. In conclusion, epitaxial LSCO thin film is a more promising choice than LSMO for use as cathode in thin film SOFC.

 $Ce_{0.8}Gd_{0.2}O_{2-\delta}$ thin films were fabricated on different substrates and at different


deposition temperatures by PLD. The 45 degree twisted epitaxial growth and cube-on-cube epitaxial growth of CGO thin films were achieved at deposition temperature of 650 °C on LAO and MgO, respectively. The FWHM of $Ce_{0.8}Gd_{0.2}O_{2-\delta}$ (200) grown on LAO is only 0.39°. Those grown on MgO substrates, however, show a FWHM of 2.35°, suggesting poor crystallinity. For the CGO thin film grown on fused silica at 650 °C, a few weak diffraction peaks are observed. This implies that the CGO/fused silica film is of polycrystalline structure. The crystallinity of the films grown on LAO and MgO at lower substrate temperature is even worst because no CGO diffraction peaks are observed. For the Ce_{0.8}Sm_{0.2}O_{2- δ} thin films, it showed similar results as that of the CGO thin films.

The electrical properties of the CGO and CSO films were measured by a two-probe DC technique as a function of temperature ranging from 400 °C to 650 °C. At the measuring temperature of 600 °C, electrical conductivity of 0.94 S/cm was achieved for the epitaxial CSO films grown on LAO at a substrate temperature of 650 °C. The film grown on the same substrate at 300 °C shows a conductivity of only 0.2 S/cm. For the CSO films and CGO films grown on MgO, the electrical conductivity tends to increase with the substrate temperature. Both materials grown on fused silica exhibit similar electrical conductivity to that of the films grown on MgO at 650 °C. In contrast to the bulk targets, enhancement in electrical conductivity of two to three orders of magnitude of is achieved in thin films, depending on the choice of substrates. To confirm the electrical conductivity to be purely ionic conduction, AC impedance measurement was carried out. Our results show that all the films



fabricated on MgO and fused silica substrates exhibit pure ionic conduction at temperatures up to 650 °C. Ionic conduction is however verified in the temperature range of 400 °C to 450 °C for films grown on LAO substrate. The electronic conduction in LAO substrate becomes significant at temperatures at and above 500 °C. Our results have suggested that the better is the crystalline quality of the film, the higher is the ionic conductivity. However, a drawback of CGO and CSO is that their intrinsic electronic conductivity is relatively high in reducing atmosphere. Hence, it is not suitable for use as electrolyte in SOFCs. Nevertheless, it can be used as a buffer layer in between the electrode and electrolyte material. The reason is that the CGO and CSO are less reactive with the perovskite oxides than LSGMO. Therefore, CGO and CSO can be used as an interlayer between LSGMO and the more active cathode of LSCO.

Epitaxial $La_{1-x}Sr_xGa_{1-y}Mg_yO_{3-\delta}$ and randomly oriented polycrystalline $La_{1-x}Sr_xGa_{1-y}Mg_yO_{3-\delta}$ thin films have been successfully fabricated on LAO substrates at deposition temperatures of 730 °C and 500 °C, respectively. According to the rocking curve, the FWHM of $La_{1-x}Sr_xGa_{1-y}Mg_yO_{3-\delta}$ (200) is determined to be between 0.4° and 0.8° depending on the doping concentration. It reveals that a very good crystallinity of the $La_{1-x}Sr_xGa_{1-y}Mg_yO_{3-\delta}$ film exists. Based on the ϕ scans, it is clear that cube-on-cube epitaxially grown $La_{1-x}Sr_xGa_{1-y}Mg_yO_{3-\delta}$ film on LAO substrate is obtained at a deposition temperature of 730 °C. No $La_{1-x}Sr_xGa_{1-y}Mg_yO_{3-\delta}$ peak was observed for the films grown at 500 °C, suggesting that the crystal structure of the $La_{1-x}Sr_xGa_{1-y}Mg_yO_{3-\delta}$ films grown at this temperature is either amorphous or randomly oriented polycrystalline.



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Among the various deposition parameters, the choice of substrate is important in controlling the structure and quality of the grown films. By fixing the temperature at 730 °C, the films were deposited on two different substrates, MgO and fused silica. The crystallinity of the as-grown films was examined by XRD. We have revealed that only reflection peaks of MgO and Pt are observed. It implies the crystallinity of the La_{1-x}Sr_xGa_{1-y}Mg_yO_{3-δ}/MgO and $La_{1-x}Sr_xGa_{1-y}Mg_yO_{3-\delta}$ /fused silica samples is poor.

Electrical properties of the La_{1-x}Sr_xGa_{1-y}Mg_yO_{3-δ} thin films grown on different substrates and deposited at different temperatures have been investigated through the DC conduction measurement. Results show that the epitaxial LSGMO thin films exhibit superior ionic conductivity than the polycrystalline LSGMO thin films. Also, La_{0.8}Sr_{0.2}Ga_{0.8}Mg_{0.2}O_{3-δ} possessed the highest conductivity of 0.74 S/cm at 600 °C. As in a conventional SOFC a viable oxide electrolyte need to possess at least 0.1 S/cm ionic conductivity at 800 °C. The present results suggest that the La_{0.8}Sr_{0.2}Ga_{0.8}Mg_{0.2}O_{3-δ} thin films should have great potential as thin film SOFC electrolyte operating at below 600 °C.

As a major step towards developing prototypes of single chamber thin film SOFCs. we have fabricated bi-layer structure of La_{0.7}Sr_{0.3}CoO₃/La_{0.8}Sr_{0.2}Ga_{0.8}Mg_{0.2}O₃₋₈/LAO and tri-layer structure of Pt/La_{0.8}Sr_{0.2}Ga_{0.8}Mg_{0.2}O₃₋₈/ La_{0.7}Sr_{0.3}CoO₃/LAO by PLD method. Based on the XRD and the TEM studies the bi-layer system shows high quality heteroepitaxy. The tri-layer system, however, displays no sign of epitaxial relationship. At present we do not know the exact reason. The deposition sequence and the



thermal history of the deposited films may contribute to such structural deterioration. Nevertheless the dark field images of the tri-layer heterostructure do reveal LSCO and LSGMO grains to possess the same orientation. As a result, there is a good chance to fabricate epitaxial LSGMO/LSCO/LAO heterostructure by careful tuning of the deposition conditions.

For the future work, we would like to achieve single chamber solid oxide fuel cells (SC-SOFCs) that operate at low temperature of about 500 °C. Conventional fuel cells rely on the strict separation of the oxidant and the fuel in order to prevent parasitic side reactions. Therefore, the cost is high due to the processes and technologies required for hermetic sealing the cell chambers at high temperatures. SC-SOFCs offer the possibility to simplify SOFC designs because only one gas compartment is necessary. Both anode and cathode are exposed to the same mixture of fuel and oxidant. However, the efficiency may be degraded. With the use of the thin film SOFC, the ionic conductivity is enhanced in the electrolyte. Our results do demonstrate that such enhancement is significant even at low temperatures close to 500 °C. Therefore, we would like to fabricate epitaxial bi-layer and tri-layer SOFC with appropriate configuration to optimize the FC efficiency. By filling proper amount of the fuel gases (oxygen and methane), the I-V characteristic of the thin film SOFC can be evaluated. All these represent the next phase of work that can lead to workable prototype development.



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