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PULSED ELECTRON DEPOSITION OF $LaMnO_3$ THIN FILMS WITH TARGET MADE OF $LaMnO_3$ NANO-POWDER SYNTHESIZED BY SELF-COMBUSTION METHOD

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ABSTRACT

$LaMnO_3$ nano-powder (LMO) was synthesized by combustion method assisted with microwave irradiation using glycine and nitrate salts of La and Mn as precursors. The LMO powder was pressed and annealed at 1000°C for 8 hours to make target for thin film deposition. The structure and element analysis were obtained by X-ray diffraction (XRD) and energy dispersive X-ray spectra (EDS). Thin films of LMO were fabricated using pulsed electron deposition (PED) at room temperature. The effects of voltage, oxygen/argon flux ratio... on the properties of thin films were studied.
Keywords: $LaMnO_3$, thin films, pulsed electron deposition, target.

INTRODUCTION

In recent times, the exhaustion of fossil fuels and environment pollution are the most urgent problems. Therefore, production and application of clean fuels become necessary for the development of human society. In particular, solid oxide fuel cells (SOFCs) have been extensively studied and attracted much attention as a promising way to generate electricity at high efficiency and low cost. The cathode material must satisfy several requirements such as: good electrical conductivity, porous structure, and chemical stability at high temperature, thermal expansion coefficient that suited with that of solid electrolyte. Most of requirements listed above are satisfied by $LaMnO_3$, make it one of the most suitable materials for cathode in SOFCs.

$LaMnO_3$ thin films can be manufactured by a variety of methods such as sputtering, pulsed laser deposition (PLD), molecular beam epitaxy... Pulsed Electron Deposition (PED), which is also a physical thin film deposition technique with great advantages: simple process, saving time, high film homogeneity and low cost, however is not well studied for preparation of perovskite thin films. In this paper, we report the fabrication of $LaMnO_3$ (LMO) thin films by PED which can be applied as cathode material in the SOFCs to demonstrate the potential of PED as a perovskite thin film deposition technique.

$LaMnO_3$ nanopowder was prepared by self-combustion assisted with microwave irradiation where glycine was used as a fuel in combustion reaction. The LMO powder was pressed and annealed at 1000°C for 8 hours to make target for thin film deposition. We investigated effect of discharge voltage and N_2/O_2 flux ratio on properties of LMO thin films through X-ray diffraction (XRD), Scanning electron micrographs (SEM) and Energy dispersive X-ray Spectra (EDS) and Raman microscopy.

EXPERIMENT

$LaMnO_3$ nanopowder was prepared by microwave irradiation method. Analytical grade La_2O_3 (99.99%), $Mn(NO_3)_2.4H_2O$ (99%) and glycine NH_2CH_2COOH (99%)) were used as the starting materials. Stoichiometric amounts of La_2O_3 was dissolved in a HNO_3 acid to obtain $La(NO_3)_3$ solution. Then, $La(NO_3)_3$ and $Mn(NO_3)_2.4H_2O$ were dissolved into deionized water at molar ratio of 1 : 1 and followed by drop-wise adding of appropriate amount of amino acide to the solution. After heating on a

hot plate at 150℃, the light pink solution evolved into a colorless transparent one and then viscous brown gel. Gel was stored in a glass container covered with an opened lid and then introduced into a microwave oven. After a few seconds, the viscous gel bubbled up and auto-ignited, with the rapid evolution of a considerable volume of colorless gases to produce black fluey powder.

The LMO powder was pressed and annealed at 1000°C for 8 hours to make target for thin film deposition by Pulsed Electron Deposition (PED). All the $LaMnO_3$ films were deposited on glass and silic substrate with the repetition rate of pulses maintained at 5 Hz, pulse width of 100 ns and 20.000 pulses. The deposition of the LMO-1 films was carried out at room temperature and at five discharge voltages: 11, 12, 13, 14 and 15 kV. The N2 and O2 gas were introduced at a pressure of 9.10-3 Torr for enhancing the electron beam and stabilizing the beam propagation to the target with 10 sccm and 15 sccm of oxygen and nitrogen, respectively.

During deposition process, the pressure was maintained by controlling the balance between the rate of high vacuum pump and the flow of oxygen and nitrogen gas introduced into chamber. The as-deposited thin films were annealed at 400, 600 and 800°C for 2h. The thin films were characterized by XRD and SEM.

RESULTS AND DISCUSSION

The XRD analysis of the $LaMnO_3$ nanoparticles with different glycine – molar ratio show the presence of perovskite phase ($LaMnO_3$) and La_2CO_5 phase. The formation of La_2CO_5 phase show the decomposition of pperovskite phase, this phase is not desirable for the cathode of the SOFC. A pure perovskite is necessary as the cathode material for the good performance of the fuel cell. Therefore, this samples were annealed at high temperature to remove the La_2CO_5 phase.

The $LaMnO_3$ nanoparticle with F=3, 3.5 were the best, so this sample were annealed at 1000°C in 8 hours. Figure 22 shows XRD patterns of $LaMnO_3$ samples with F=3, 3.5 (glycine as fuel) before and after anneling of 1000°C at 8 hours. It can be seen after annealing, diffraction peaks were narrower, stronger and pure.

The crystalline sizes of the samples increase clearly after annealing as expected due to the crystall growth during annealing process at high temperature. It should be noted that after annealing a clear peak shift to higher angle was observed.

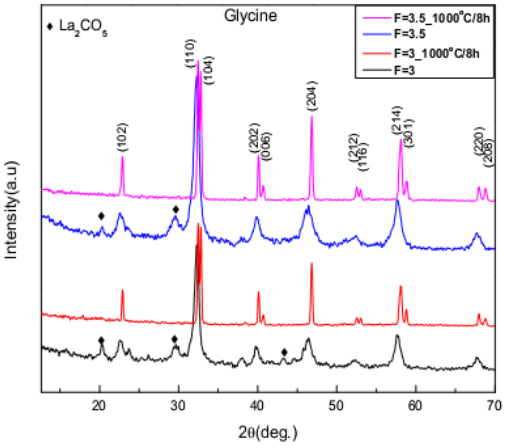

Figure 1. XRD patterns of $LaMnO_3$ samples with F=3, 3.5 before and after annealing of 1000°C/8h

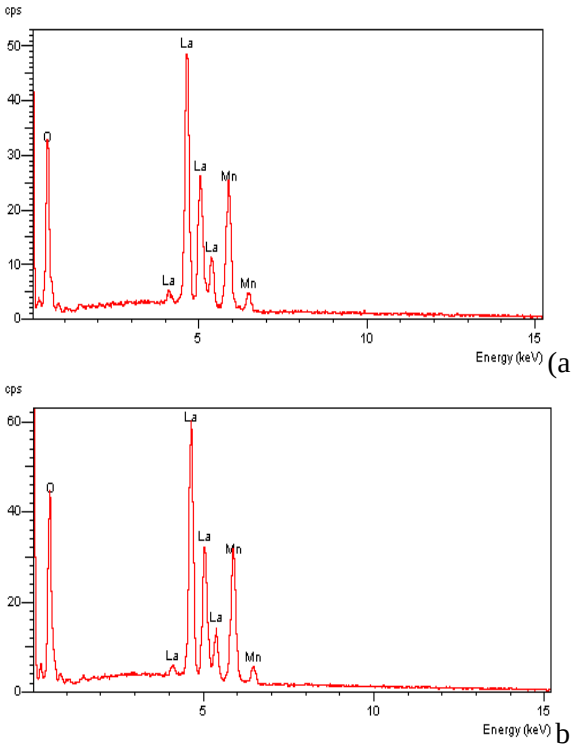

Figure 2. EDS spectra of the $LaMnO_3$ nanopowder with F=3 (a) before and (b) after annealing at 1000°C

An according decreasement of lattice parameter are shown in Table 1. The results imply that anealing the samples at 1000°C does not result in transition of phase structure. However, the change in the lattice parameter suggests that annealing phase transition from hexagonal to other structure can occur at higher temperature or in longer time.

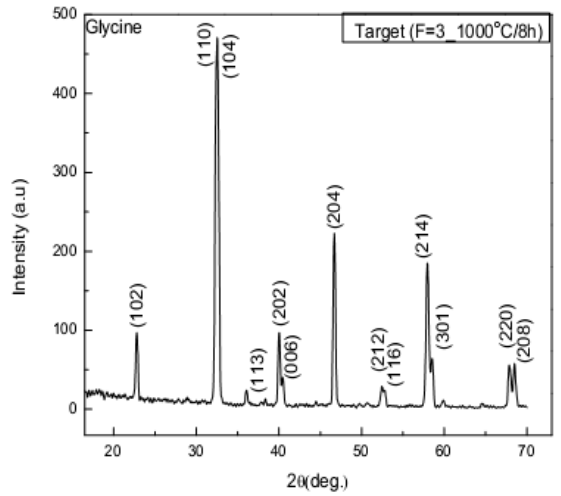

Figure 3. XRD pattern of $LaMnO_3$ target made of $LaMnO_3$ nanoparticles.

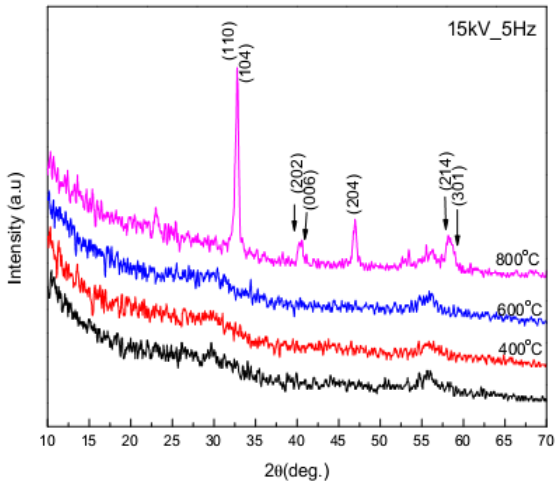

Figure 5. XRD patterns of the $LaMnO_3$ thin films deposited before and after annealing 400°C, 600 °C and 800°C at 15kV.

After fabrication powder, we chose sample has molar ratio glycine/nitrat F=3 with glycine as fuel to create target becausethe results of this sample are very good and suitable for thin film formation. The LMO powder was pressed and annealed at 1000°C for 8 hours to make target. The structure and phase purity of LMO target was examined by XRD measurements as shown in Figure 3. The XRD patterns reveal that the asprepared LMO target has hexagonal structure. The LMO target showed peaks corresponding to reflection from (102), (110), (104), (202), (204), (212), (214) and (220) planes, where (110) and (104) peaks have the strongest intensity clearly demonstrate the preferred crystal growth during annealing process.

Using nanopower of LMO to make target helps to reduce the treating temperature to 1000°C, while target preprared by solid state reaction normally required much higher annealing temperature (1300-1400°C) and longer time (12-24h).Figure 4 shows XRD patterns of the $LaMnO_3$ thin films deposited at 15kV before and after annealing at different temperature.

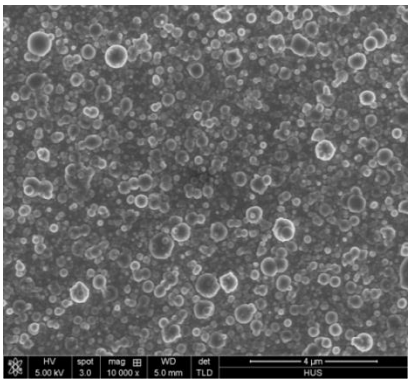

Figure 6. SEM images of LMO thin films deposition at 15 kV after annealing at 800°C.

It can be seen, the as deposited films and films annealed at 400°C and 600°C were in amorphous nature and no diffraction peaks appeared. The intensity of diffraction peak at 2θ = 32.423° corresponding to the peaks of LMO increased after increase annealing temperature up to 800°C. The crystalline of thin films after annealing at 800°C are of the same structure as target.

Table 1. The lattice parameter of the $LaMnO_3$ samples with different ratios of glycine/nitrate molar F=3, 3.5 before and after annealing at1000 °C for 8h.

Sample	Latticestructure	a(Å)	b(Å)	c(Å)	Volume of unit cell ($Å^3$)
F=3	Hexagonal	5.54	5.54	13.46	357.66
F=3_1000 °C	Hexagonal	5.51	5.51	13.29	349.43
F=3.5	Hexagonal	5.54	5.54	13.47	357.62
F=3.5_1000 °C	Hexagonal	5.51	5.51	13.28	351.17

SEM images of thin films deposition at 14 kV, 15kV after annealing different temperature show that the partice size distribution is quite uniform.

CONCLUSION

$LaMnO_3$ nano powder was successfully synthesized using combustion assisted with microwave irradiation method. Ratio of amino acid/nitrate (F) is critical to the formation of the product. Optimum value of F to give highest quality product is dependent upon used amino acid and F=3÷3.5 for glycine. $LaMnO_3$ thin films were prepared by PED method on glass/silic substrate at room temperature at five discharge voltages: 11, 12, 13, 14 and 15 kV. The obtained films were amorphous, and could be converted into crystalline phase after annealing at 800 ^oC.

Acknowledgment

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