Coating of nano sized ionically conductive films by sol-gel route

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ABSTRACT

Precursors were dissolved for preparation of LaMnO$_3$-$\delta$ and La$_{0.8}$Ca$_{0.2}$MnO$_3$-$\delta$ films were prepared by sol-gel dip coating routes. Precursor solutions were synthesized from all nitrate salts of the respective cations (La, Mn and Ca), using methanol as solvent and Acetyl Acetone as chelating agents. After having the red transparent solution, it was stirred for 12 hours before coating. Ultrasonically cleaned substrate is dipped into the solution and taken immediately into vertical furnace which is preheated at 550 °C. A dense amorphous film is coated on the Al$_2$O$_3$ substrate. Crystallization of the films was carried out between 800 and 900°C. Oriented polycrystalline films of both LaMnO$_3$-$\delta$ and La$_{0.8}$Ca$_{0.2}$MnO$_3$-$\delta$ were grown on the (0001)-oriented Al$_2$O$_3$ substrates. These films were characterized by means of XRD, SEM, and AFM. Conductivity measurement of the films was conducted via Van Der Pauw method.

1. Introduction

Thin film solid oxide fuel cells (SOFCs) have attracted world-wide research interest because of its high conversion efficiency, as well as environmental compatibility. Solid oxide fuel Cells (SOFC) have exceptional potential for use as electric power generation systems, because of their high energy conversion efficiency which can reach up to 65%. SOFCs have many advantages such as multi-fuel capability and simplicity of system design. Furthermore, the exhaust heat can be used as a heat source for a variety of processes. [1].

The cathode materials must be stable in the oxidizing environment, have good electronic conductivity and sufficient catalytic activity for oxygen reduction under operating conditions. Many types of cathode materials have been examined. Some
complex oxides in the perovskite family may satisfy the requirements with regard to electrical conductivity.

Sr-doped lanthanum manganite (LSM) is considered to be a suitable cathode material for solid oxide fuel cell (SOFC) because of its high electronic conductivity, high catalytic activity for oxygen reduction, and chemical and mechanical compatibility with solid electrolytes based on yttria-stabilized zirconia. (1). 

At present, perovskite structured oxides based on LaMnO$_3$ doped with SrO and CaO are mostly used as cathode material [2] due to their high electrical conductivity and compatibility with the solid electrolyte, generally Y$_2$O$_3$ doped-zirconia. Many investigations have been carried out with regard to the choice of materials and processing techniques (2). However, there are few processes that can be used to fabricate high performance cells quickly and inexpensively. Sol-gel deposition has been used to deposit many oxide layers for different application as well as the cathode material of LaCoO$_3$ (3-9). 

This paper is thus focused on the coating and characterization of LaMnO$_3$ thin film on Al$_2$O$_3$ single crystal by using sol-gel route. 

2. Experimental 

2.1. Solution Preparation

All nitrate precursors were used as starting materials. Lanthanum, Manganese, Strontium and Calcium nitrates were used as needed. Acetyl acetone and methanol were used as chelating agent and solvent respectively.

Three different solutions were prepared; LaMnO$_3$, La$_{0.8}$Sr$_{0.2}$MnO$_3$ and La$_{0.8}$Ca$_{0.2}$MnO$_3$. Precursors, chelating agent and solvent were put together after weighing the proportional amounts. La was substituted with 0.2 ratios of Sr and Ca for the La$_{0.8}$Sr$_{0.2}$MnO$_3$ and La$_{0.8}$Ca$_{0.2}$MnO$_3$ solutions respectively. The mixture was mixed on a magnetic stirrer for 24 hours then a pink and completely transparent solution was received.
2.2. Coating of amorphous film

(0001)-oriented Al₂O₃ substrates with dimension of 20 mm x 20 mm x 0.5 mm was dipped into the solution then taken into the vertical tube furnace which was preheated at 600 °C. Films were coated by dipping two or three times into the solution. After each dipping, it was fired in preheated furnace then dipped again. The forming of the film is schematically shown in figure 1.

![Schematic of the steady-state dip-coating process](image)

Fig. 1. Schematic of the steady-state dip-coating process, showing the sequential stages of structural development that result from draining accompanied by solvent evaporation and continued condensation reactions (3).

Then the coated films were annealed at 1025 C for 30 minutes in the air.

3. Characterization of Films

3.1. Atomic Force Microscopy

Amorphous coating revealed a needle-shape view from the surface. Homogeneous very thin and long grains were scanned by AFM profilemeter. The coating has a crack and pin-free surface. The surface profile of non-annealed film is given in figure 2.
The surface morphology and the grain size of the films annealed at 1025 °C were inspected by AFM. The average grain size of crystalline films was estimated to be 45 nm from the AFM images. The crystalline film looked uniform and crack-free as well pore-free, mainly consisting of the equaxed packed fine grains (Fig. 3). The AFM image of two-times dipped film also showed same morphology on Al₂O₃ single crystal substrate (Fig. 4). However, it is clearly seen from the AFM images that the more the dipping number, the larger the grains.

Figure 3. AFM surface morphology of sol-gel coated LaMnO₃. Film was annealed at 1025 °C
Figure 4. AFM surface morphology of two-times and three-times dipped sol-gel coated LaMnO$_3$ films. Films were annealed at 1025 °C

3.2. SEM and FIB Examinations

Coated film surfaces were also examined by means of SEM. The SEM examinations show that the film was pore and crack free. The coating is homogeneous and the grains were distributed evenly (figure 5).

Figure 5. SEM image of the coated LaMnO$_3$ film

Film thickness was measured by ionically etching the coated film. As it is seen from figure 6, coated surface of the film was etched ionically by focused ion beam (FIB) then tilted 53° in the vacuum chamber of the SEM. It can be seen from the image, which is taken from the etched and tilted surface, that film thickness about 120 nm.
The examined film was coated by dipping two times so the film thickness for each dip can be said as 60-70 nm.

Figure 6. SEM image of the ionically etched section of the two times dipped film.

3.3. Crystallographic Examinations

Crystallographic structure of the coating was characterized by means of XRD. Coated films were amorphous after firing at 500 °C. Films were fully crystallized after annealing at 1025 °C. Annealing at 975 °C, gave a peak which belongs to the LaMnO$_3$ phase but it is not a clear peak. The XRD peaks of the annealed films are given in figure 7. LaMnO$_3$ peaks appeared clearly after annealing at 1025 °C at two theta angles of 30, 32.8, 39.7 and 47.2.
3.4. Conductivity measurement

The planar electrical conductivity of coated sample was measured using a DC four-point (Van der Pauw) in air from room temperature to 925°C. Figure 8 shows the resistance vs temperature graph. It is commonly known that the energy barrier to ion movement is high at low temperatures and for most ceramics at room temperature. However, thermal vibrations move ions further and further away from their equilibrium state as the temperature is increased. These kinds of materials become ionically conductive once the thermal energy is high enough for a specific material for ions to move over the energy barrier under the influence of an electric field. The degree of ionic conductivity then increases as the temperature further increases [10].

It is seen from the figure that, while the resistance of the film start to decrease at about 500 °C. The resistance of the film decreases continuously with increasing temperature.
4. CONCLUSIONS

Coating of ceramic films using sol-gel has promised in depositing dense and homogenous films of the cathode systems for SOFCs cost-effectively. The deposited films cling to the substrate very well. Figures 2-5 show the surface morphology of the coated layer. The particle size of the as-deposited dense LaCoO$_3$ film is around 60 to 80 nm and the total thickness of the film is approximately measured to be 80 nm per dipping. This study shows that high quality, crack free and highly dense LaCoO$_3$ thin films can be fabricated using sol-gel.

References


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