# Nanostructured LZO Films: Synthesis and Characterizations

H. S. Chen [*], R. V. Kumar[**] and B. A. Glowachi[***]

Department of Materials Science and Metallurgy, University of Cambridge, Pembroke Street
Cambridge CB2 3QZ, U.K.
[*]hsc28@cam.ac.uk
[**] rvk10@cam.ac.uk
[***] bag10@cam.ac.uk

## ABSTRACT

Nanocrystalline lanthanum zirconium oxide (LZO) films have been successfully synthesized by a wet-chemical route, using dried lanthanum acetate, zirconium propoxide, propoionic acid, acetic acid glacial, and anhydrous methanol. X-ray 2θ-scan diffraction patterns of the LZO film deposited on the Ni/W substrate displayed only the (400) peak. X-ray ω-scan diffraction data showed that the LZO films exhibited out-of-plane alignment along <400>. Field emission gun scanning electron microscope images have indicated that LZO films are composed of nanoparticles with an average size of about 25 nm. The Taguchi Design has been employed to examine the effects of composition and solution chemistry of the precursors in the synthesis of LZO. The optimum experimental conditions have been evaluated as: 0.7±0.5 for the ratio of the lanthanum acetate to the propionic acid, 0.08±0.02 mol/kg for the precursor concentration, and 850±10 $^{o}$C for the heating process using 5±1 $^{o}$C per minute.

***Keywords***: LZO, Nanocrystalline, film

## 1 INTRODUCTION

Development of new synthesis methods for nanostructured materials and demonstration of improved and/or unusual properties of these materials have increased rapidly within recent years. Nanostructured materials are available in a variety of compositions of metal oxides and as metals supported on metal oxides or vice versa, which have led to many investigations of their exceptional chemical, physical and electric properties.

The attractiveness of the sol-gel method of synthesis arises from the fact that virtually any metal oxide system can be examined, and no special equipment as such is required. Sol-gel methods comprise of precipitation of nano-scaled colloid suspension of particles from a solution formed by dissolving a salt in a suitable liquid, usually water, which is then modified by addition of an acid or a base to obtain a gel network. Alternatively, it is also common to use polymeric alkoxide route, where a metal oxide is dissolved or supported in a suitable liquid usually alcohol, which is then activated by an acid or a base resulting in a gel network.

Lanthanum zirconium oxide ($La_2Zr_2O_7$ or LZO) is a well known material with a pyrochlore.structure[1] In fact, LZO has two different crystal structures, one is cubic fluorite type, and the other is cubic pyrochlore type. The LZO is thought to be a potential candidate for applications as high dielectric constant materials in the Si-based industry, thermal barriers, radiation resistant layer and others.[2] In the past decade, the number of the scientific reports about the synthesis and the properties of LZO has been growing rapidly. This study reports a sol-gel synthesis method to obtain a nanocrystalline LZO film and Taguchi Design statistical method has been used to optimise the film.

## 2 EXPERIEMNTAL

### 2.1 Preparation of LZO Precursor

Lanthanum acetate hydrate powder (99.9%, Aldrich) was first dried at 170$^{o}$C for an hour. Zirconium (IV) propoxide (70wt%, Aldrich), propoionic acid (99.5%, Fluka-Garantie), acetic acid glacial (analytical reagent grade, Fisher), and methanol anhydrous (99+%, Aldrich), all as liquids were used as received. LZO precursor sol was prepared in a stoichiometric ratio of La and Zr. Lanthanum solution was first prepared by dissolving dried lanthanum acetate in propionic acid at a temperature near 80 $^{o}$C. The solution was then cooled to room temperature after it transformed to a clear liquid. Zirconium solution was prepared by rapidly adding glacial acetic acid into zirconium propoxide and then was mixed by a magnetic stirrer for 15 minutes. The zirconium solution was then added into the lanthanum solution and mixed by the stirrer for another 30 minutes. The LZO precursor sol was obtained eventually by diluting the above mixture with methanol to a concentration of 0.2 mol/kg.

### 2.2 Preparation of LZO Film

For the coating process to deposit a LZO film, the precursor sol was first diluted to a desired concentration and then loaded into the ink-jet printing system. A substrate, which was cleaned in an ultrasonic system sequentially by ethanol and acetone and thermally treated


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at 850 °C to remove all organics, was placed 30 mm below the nozzle. The precursor solution was loaded into a reservoir in the ink-jet printer, and pressure was applied to the reservoir by a mechanical pump.[3] A computer-controlled electronic system was used to allow the nozzle to open for a fixed time period so that a set amount of an ink could be deposited. LZO films were printed as a 5x25 $mm^2$ track on textured Ni substrates of 5x40 $mm^2$ at room temperature under ambient atmosphere. The sample was then moved to a pre-purged furnace heated at 10 °C/min to 900°C for 1 hour under Ar-5%-$H_2$ atmosphere and then cooled in the furnace which was switched off.

## 2.3 Characterization

Weight change as a function of temperature of the lanthanum acetate, LZO precursor solutions, and dried LZO precursor solution films, were examined by thermogravimetry analysis (TGA, TA Instruments Q500). Spectroscopy of the lanthanum acetate, the zirconium propoxide, the as-prepared LZO precursor solution and both the dried and the thermally treated LZO precursor films , were carried out by Fourier transform infrared (FTIR, Bruker Optics Tensor 27 FT-IR) spectrometer. X-ray diffractometer (Phillips PW 1830/00 with Cu K radiation) was employed to analyze the crystal structure and also the out-of-plane texture of LZO films. The 2-θ scan was used to examine the crystalline phase of the LZO films. Out-of-plane orientation was judged by estimating the FWHM (expand this) values of the diffraction peaks obtained from the $\omega$ -scan mode at a fixed 2θ value with 1/12° of diversion slit. The better the out-of-plane texture, the narrower the FWHM of the diffraction peak from the $\omega$-scan. The surface morphology of the LZO films was investigated by field emission electron scanning microscope (FEGSEM, JEOL 6340F) with a working distance of 6 mm and an acceleration voltage of 5 keV. In the current study, surface integrity was defined as a ratio of Vs to Vf, which are the area of a solid part and the total area of the film, respectively, calculated by ImageJ version 1.37.

# 3 RESULTS AND DISCUSSIONS

Figure 1 gives the FTIR spectra of the LZO precursor mixture and LZO precursor film (dried overnight at room temperature) along with the zirconium propoxide and the lanthanum acetate hydrate data. Not only the LZO precursor mixture but also the dried LZO precursor films exhibited a similar characteristic to a combination of the patterns of the zirconium propoxide and the lanthanum acetate hydrate, implying there was no significant change in bonding at the molecular level among elements after LZO precursor was formed, though some of the peaks were slightly shifted and several extra peaks had appeared that can be ascribed to the formation of complexes.

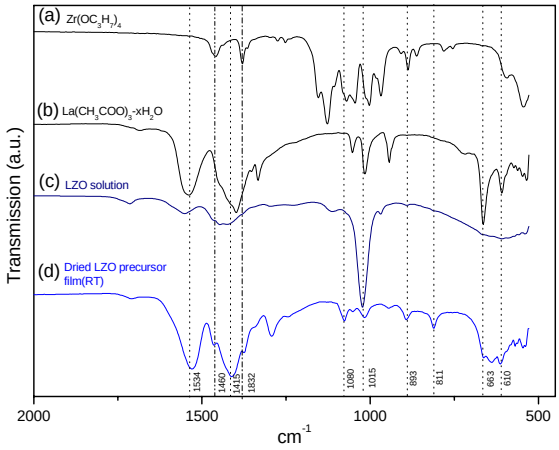



Figure 1: FTIR spectra of chemicals and LZO precursors

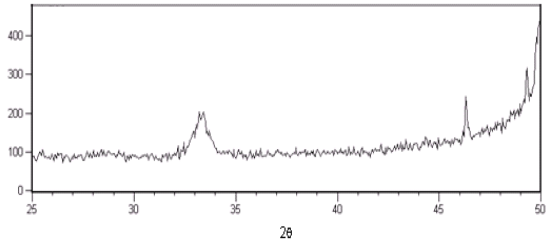



Figure 2: XRD of LZO film.

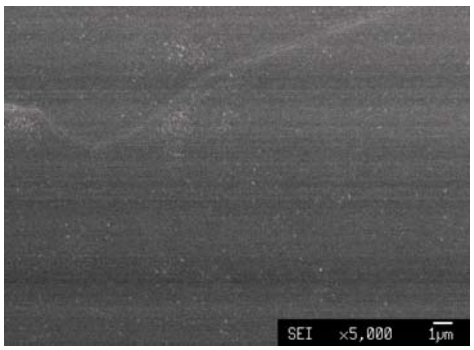
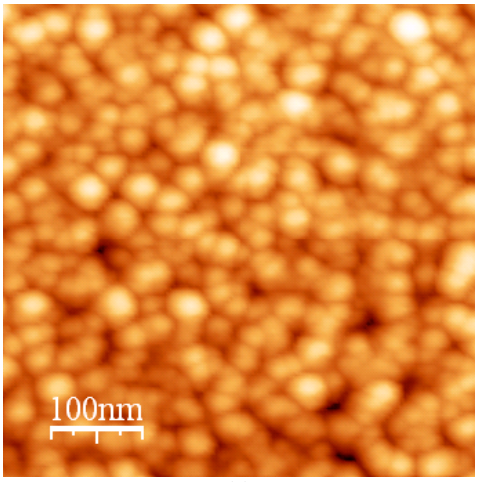
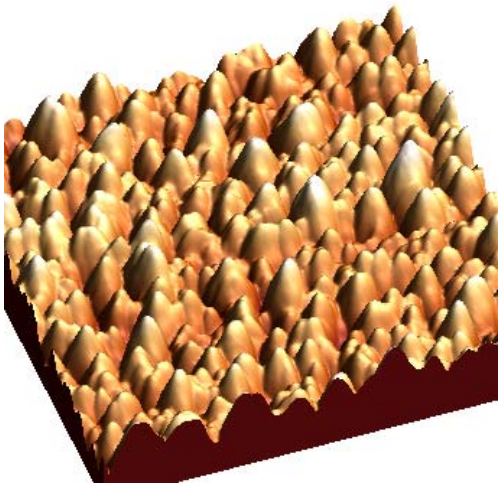



Figure 3: FEGSEM images of a LZO film.

Figure 2 shows a XRD pattern of a LZO film on the Ni substrate after heating at 900 °C for an hour. The pattern has lost some diffraction peaks such as (111) and displays only a (400) peak. This indicates that the LZO film have a lattice alignment along <400> directions. FEGSEM images of the LZO film after the heating process are shown in Figure 3. The LZO precursors formed a dense film containing nanocrystallites with a size of about 25 nm, but generated some pine holes on the surface. Figure 4 (a) and (b) provide a display of the AFM images of a LZO film. The images clearly show that the LZO films are composed of nanoparticles, which are conical in shape with the cone being perpendicular to the substrate surface. As can be observed, the nanocrystlaline LZO have grown as individual cones along the c-axis, giving visual evidence for the XRD data.




(a)



(a)

Figure 4: AFM image of a LZO film.

## 4 TAGUCHI DESIGN

The LZO precursor preparation contains at least eight components in the system. Given the number of steps in the subsequent heating process there were at least ten factors. So it was difficult to clarify the role of each factor in the solution, and also difficult to adjust experimental conditions to gain better results by trial and error. To investigate experimental variables, Taguchi Design was employed for the current study.

The following major factors have been identified in the synthesis of LZO: ratio of lanthanum acetate to propionic acid; concentration of diluted solution used in the coating system; heating temperature; and the heating rate. Thus for four control factors and three factor levels, the $L^9(3^4)$ orthogonal array was employed in our study. Other variables including mixing conditions of La solution and Zr solution were fixed to reduce the overall complexity in this analysis. Detail discussion will be published elsewhere.

| Control / Factors / Levels | Cn (mol/kg) | Ratio of $La(Ac)_3$ to Propionic Acid | Heating Rate (°C/min) | Heating Temp. (°C) |
|---|---|---|---|---|
| | A | B | C | D |
| *1* (Low) | 0.05 | 0.7 | 1 | 850 |
| *2* (Medium) | 0.08 | 1.0 | 5 | 900 |
| *3* (High) | 0.1 | 1.3 | 10 | 1000 |

Table 1: Chosen control factors and levels.

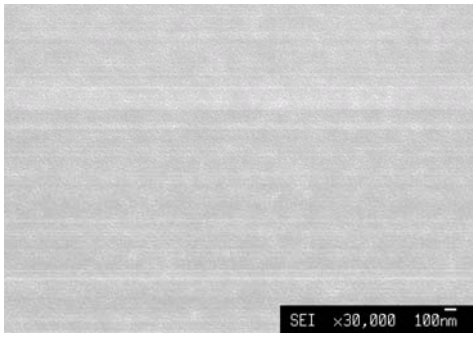



Figure 5: FEGSEM images of a LZO film (for Taguchi Desgin).

The optimum experimental conditions given from Taguchi design are: 0.7±0.5 for the ratio of lanthanum acetate to propionic acid, 0.08±0.02 mol/kg for the precursor concentration, and 850±10 °C for the heating process at a heating rate of 5±1 °C per minute. As shown in Figure 5, the LZO film, corresponding to the optimum parameters is of a good quality and free of pin hole with a surface integrity value of 0.99.

## 5 CONCLUSIONS

A dense, smooth, pin-hole-free lanthanum zirconium oxide films have been successfully synthesized by using ink-jet printing from a liquid ink prepared by dried lanthanum acetate, zirconium propoxide, propoionic acid, acetic acid glacial, in anhydrous methanol. The Taguchi Design has successfully been employed to find the optimum experimental conditions, which are 0.7±0.5 for the ratio of the lanthanum acetate to the propionic acid, 0.08±0.02 mol/kg for the precursor concentration, and 850±10 °C for the heating process using 5±1 °C per minute. The LZO particles are conical in shape and are textured along the c-axis.

## REFERENCES

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