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ORIGINAL PAPER

Study on chemical-solution-deposited lanthanum zirconium oxide film based on the Taguchi method

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Abstract A statistical route, Taguchi Design, applied to the analysis of experimental factors for coating lanthanum zirconium oxide films on metal substrates by inkjet printer is presented. The synthesis of lanthanum zirconium oxide precursor is derived from a chemical solution containing lanthanum acetate hydrate, zirconium propoxide, propionic acid, glacial acetic acid, and methanol anhydrous. Experimental factors analyzed by Taguchi Design show that the ratio of lanthanum acetate to propionic acid and the concentration of precursor used for inkjet printing are the dominant factors for the quality of films. With the deduced optimum conditions, lanthanum zirconium oxide films reveal good surface morphology and high out-of-plane alignment that is consistent with the Taguchi prediction.

Keywords Buffer layer · Inkjet printing · Lanthanum zirconium oxide · Superconductor · Taguchi

1 Introduction

In the past decade, scientific papers about synthesis and properties of lanthanum zirconium oxide ($La_2Zr_2O_7$ or LZO) have been growing rapidly [1–12]. LZO possesses two lattice structures; one is cubic fluorite type, and the other is cubic pyrochlore type. The cubic pyrochlore LZO has been thought to be a candidate in some applications such as high dielectric constant materials, thermal barriers, and radiation resistant layers [7, 8]. In addition, as the pseudo-cubic lattice parameter of the pyrochlore LZO is 3.81 Å having a small lattice mismatch of about 0.5 and 1.8% with *a*- and *b*-axis for YBCO ($a = 3.83$ Å and $b = 3.88$ Å), the LZO has been considered as a buffer layer for growing an epitaxial YBCO film [9–11].

Synthesis of epitaxial LZO films on biaxially textured Ni or Ni-W (100) substrates (lattice parameter $\sim$3.52 Å) by wet chemical sol–gel process using lanthanum methoxyethoxide and zirconium methoxyethoxide as precursors was first reported in 2000 [9]. A similar chemical-solution-deposition method, alternatively using $La(CH_3COCHCOCH_3)_3 \cdot xH_2O$ (lanthanum pentanedionate) and $Zr(CH_3COCHCOCH_3)_4$ (zirconium pentanedionate) as precursors was also presented later [10, 11]. For these wet chemical methods, LZO precursor solution was first prepared before it was coated onto Ni-5%W substrates. A subsequent thermal treatment under reducing atmosphere, for example using 5% H_2 in Ar, was carried out for the formation of LZO films with the simultaneous protection of Ni-5%W substrates from oxidation. It was found that microstructure of LZO films was strongly influenced by the speed of coating, the parameters of thermal treatment, and the gaseous atmosphere during processing [10–12]. For example, the densification of LZO films increased while the porosity of LZO films decreased as the coating rate was increased, but showed no significant change in the grain size.

On the other hand, inkjet printing system has advantages of patterning process and saving materials. It has been employed in the coating process for LZO and YBCO films, demonstrating an efficient way to produce coated conductors [13–15]. As the inkjet printer is a non-contact dot-matrix coating method where droplets of materials are jetted to a demanded position, the morphology of printed films often contains some pinholes. In fact, the defects of printed films are not only simply influenced by the

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parameters of an inkjet printer, but also strongly affected by the rheological properties of ink which are determined by the materials chemistry. Accordingly, in order to prepare high quality LZO films, experimental parameters of both inkjet coating and ink physico–chemical properties may need to be taken into account together.

This study reveals an analysis of experimental factors for the LZO film fabrication process that involves preparation of precursors by wet chemical method, inkjet coating process, and thermal treatment. In order to evaluate importance of experimental factors, we employed a statistical method, Taguchi design, to aid the evaluation of weights of selected experimental factors as conventional trial-and-error approach may be not productive and will require spending much time to find out the optimum experimental condition. Taguchi approach is a robust method for designing a process that has a minimum sensitivity to variations in uncontrollable experimental factors [16]. This method has been successfully applied in industrial processes and manufacturing in order to improve product reliability and quality. This method is also considered viable for "picking the winning combination of parameters" in developing new scientific processes. Given the large number of experimental factors and the use relatively new methods for making the coating, the Taguchi design can help us achieve the quality of the coating without the concern for eliminating variations in factors which are difficult and very time-consuming to control.

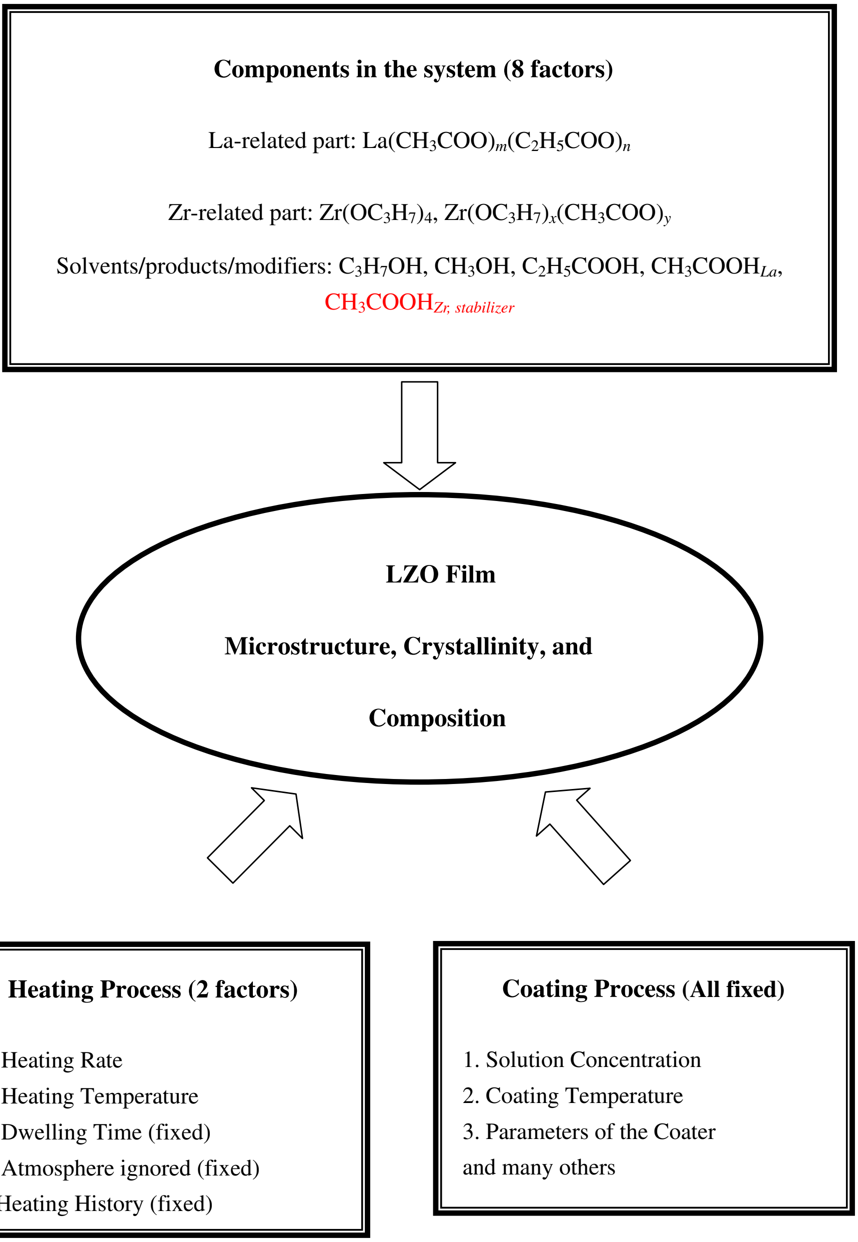

Fig. 1 Major factors in the process of LZO preparation

2 Experimental

2.1 Materials and synthesis

Lanthanum acetate hydrate powder, $La(CH_3COO)_3 \cdot xH_2O$ (99.9%, Aldrich) was first dried at 170 °C for an hour. Zirconium (IV) propoxide or $Zr(OCH_2C_2H_5)_4$ in 1-propanol (70 wt%, Aldrich), propoionic acid or C_2H_5COOH (99.5%, Fluka-Garantie), acetic acid glacial or CH_3COOH (analytical reagent grade, Fisher), and methanol anhydrous or CH_3OH (99+%, Aldrich) all as liquids were used as received.

A LZO precursor solution was prepared in a stoichiometric ratio according to the following recipe. Lanthanum solution was first prepared by dissolving the dried lanthanum acetate in a propionic acid at about 80 °C and cooled to room temperature after it transformed to a clear liquid. Acetic acid showed no sufficient solubility of the dried lanthanum acetate so propionic acid was used in the current study. Zirconium solution was prepared by quickly mixing zirconium propoxide with glacial acetic acid that acted as a stabilizer preventing $Zr(OC_3H_7)_4$ from hydrolysis. A LZO precursor solution was obtained by the dilution of a mixture of the above zirconium and the lanthanum solutions with methanol to 0.2 mol/kg.

For inkjet coating process to deposit a LZO film, the precursor solution was first diluted to a desired concentration and loaded into an inkjet printing system [14]. A substrate, which was first cleaned sequentially by ethanol and then by acetone in an ultrasonic system along with a thermal treatment at 850 °C to remove organics, was placed 30 mm below the nozzle. A computer-controlled electronic system was used to allow the nozzle open for a fixed time period so that a set amount of ink could be deposited. Nozzle opening time and inter-drop distance were set 500 μs and 4 mm, respectively. LZO films were printed as a $5 \times 25\ mm^2$ track on textured Ni-5%W substrates of $5 \times 40\ mm^2$ at room temperature under ambient atmosphere. Besides ink concentration, other parameters of the ink-jet printer were kept constant for all exercises.

The as-deposited wet film on Ni-5%W substrate was then moved to a pre-purged furnace and treated by thermal process under Ar-5%–H_2 atmosphere and cooled with furnace set to off position. The experimental conditions followed the suggestion from Taguchi design to be mentioned later in this paper. X-ray diffractometer (Philiips PW 1830/00 with Cu K radiation) was employed to analyze the out-of-plane texture of LZO films by estimating full width at half maximum (FWHM) values of diffraction peaks obtained from ω-scan mode at fixed 2θ with 1/12° of diversion slit (i.e. rocking curve at omega). The surface morphology of LZO films was investigated by field emission electron scanning microscope (FEGSEM, JEOL 6340F). The surface integrity was defined to evaluate the samples, as shown below.

$$\psi = (V_s/V_f) \quad (1)$$

where V_s and V_f are the area of a solid part and the total area of the film, respectively.

2.2 Taguchi methods

2.2.1 Variables in the system

LZO precursor solution is considered to involve six components, i.e. $La(CH_3COO)_3$, C_2H_5COOH, $Zr(OC_3H_7)_4$, C_3H_7OH, CH_3COOH, and CH_3OH. Ignoring possible chemical interactions between the La solution and the Zr solution, the chemical process of the LZO precursor can be briefly described by the following equations after system is in equilibrium.

$$\begin{aligned} &La(CH_3COO)_3 + C_2H_5COOH + Zr(OC_3H_7)_4 + C_3H_7OH \\ &+ CH_3COOH + CH_3OH \leftrightarrow La(CH_3COO)_m(C_2H_5COO)_n \\ &+ Zr(OC_3H_7)_4 + Zr(OC_3H_7)_x(CH_3COO)_y + C_2H_5COOH \\ &+ C_3H_7OH + CH_3COOH + CH_3OH \quad (2) \end{aligned}$$

where coefficients are not balanced. Given the number of steps in the subsequent annealing process there are at least ten experimental factors that have been identified that might be related to the final experimental results, as shown

Table 1 Chosen control factors and levels

Level	Cn (mol/kg)	Ratio of La(Ac)$_3$ to propionic acid	Heating rate (°C/min)	Annealing temperature (°C)
	Factor A	Factor B	Factor C	Factor D
1	0.05	0.7	1	850
2	0.08	1.0	5	900
3	0.1	1.3	10	1,000

Table 2 $L_9(3^4)$ orthogonal array (9 runs and 4 factors)

Exercise	Levels			
	Factor A	Factor B	Factor C	Factor D
1	*1*	*1*	*1*	*1*
2	*1*	*2*	*2*	*2*
3	*1*	*3*	*3*	*3*
4	*2*	*1*	*2*	*3*
5	*2*	*2*	*3*	*1*
6	*2*	*3*	*1*	*2*
7	*3*	*1*	*3*	*2*
8	*3*	*2*	*1*	*3*
9	*3*	*3*	*2*	*1*

Table 3 Standard types of the output response

Type of response	Equation	Target	Case
Smaller-the-better	$S/N_{\mathrm{S}} = -10\log\left(\frac{1}{n}\sum_{i=1}^{n} y_i^2\right)$	Reduction of system response	Distortion, number of porosity, etc.
Larger-the-better	$S/N_{\mathrm{L}} = -10\log\left(\frac{1}{n}\sum_{i=1}^{n} \frac{1}{y_i^2}\right)$	Increase of system response	Mechanical intensity etc.
Nominal-the-best	$S/N_{\mathrm{N}} = 10\log\left(\frac{\bar{y}^2}{S^2}\right)$	Approach to a target	Film thickness, window size on chips etc.

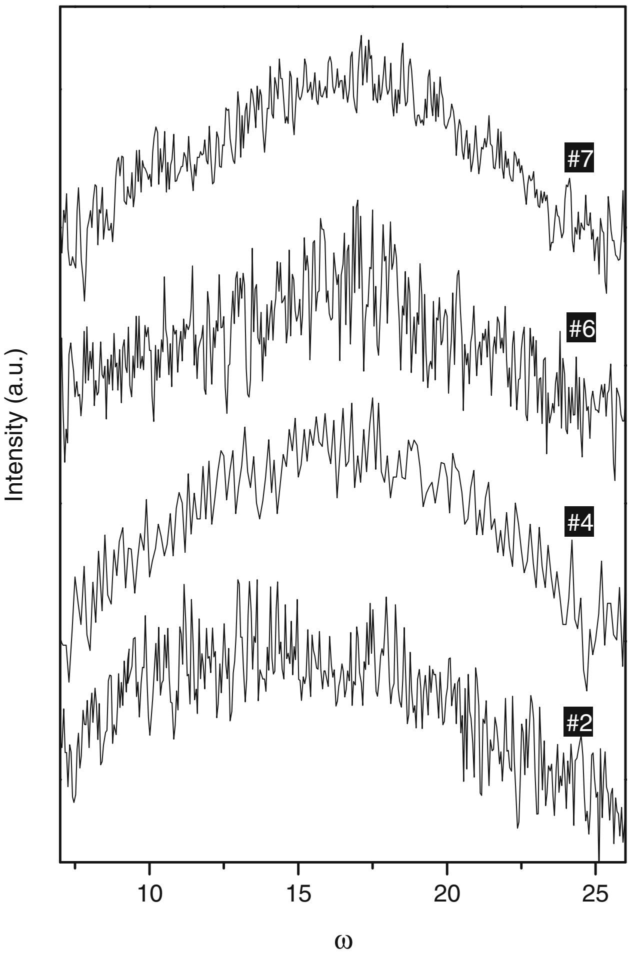

Fig. 2 XRD patterns of LZO films. The out-of-plane lattice alignment of LZO films is estimated by FWHM values of diffraction peaks in ω-scan mode

schematically in Fig. 1. So it is difficult to clarify the functions of each factor in the fabrication process, and may also take much time to obtain better experimental conditions. In order to apply Taguchi Design for the analysis of experimental parameters, predominant factors and their levels in the process must be first chosen before experimental results are transformed to statistical data.

2.2.2 Determination of control factors in the Taguchi design

Experimental factors in the synthesis of LZO are identified as following: ratio of lanthanum acetate to propionic acid; mixing time/temperature of preparation of the La solution; ratio of zirconium propoxide to acetic acid; mixing time/temperature for preparation of the Zr solution; mixing time/temperature for mixing the La and the Zr solutions; concentration of diluted solution used in the inkjet printing system; annealing temperature; and heating rate. Some variables including mixing conditions of the La solution and the Zr solution are expected to be minor and are fixed to reduce levels of complexity. Besides, it is relatively difficult to clarify the role of ratio of zirconium propoxide to acetic acid in the system as the commercial zirconium alkoxide is preserved in an alcohol, increasing the degree of difficulty when analyzing the effect of the zirconium alkoxide. Hence this factor is not considered in the analysis. Solubility of lanthanum acetate, on the other hand, is expected to be crucial in the synthesis as CH_3COO^- and $C_2H_5COO^-$ are ligands to the metal ions. Thus ratio of lanthanum acetate hydrate to propionic acid is considered a factor to be analyzed. The control factors chosen to be analyzed by the Taguchi Design are: ratio of the lanthanum acetate to the propionic acid, concentration of the precursor solution used for inkjet printing, annealing temperature, and heating rate.

Levels of the control factors are determined according to practical experimental situations. For example, ratios of the lanthanum acetate to the propionic acid is selected as an equal molar ratio, a lower level (0.7:1), and a higher level (1.3:1) that allow lanthanum acetate powder to be dissolved in the propionic acid. Concentration of precursor solution used in the inkjet printing system is limited. To avoid blocking up the nozzle, only liquids with low viscosities as represented by LZO concentrations, 0.05, 0.08, and 0.1 mol/kg are suitable for use. Heating rates are simply chosen as 1, 5, and 10 °C/min. Temperatures of subsequent annealing process are chosen as 850, 900, and 1,000 °C. Table 1 summarizes the chosen factors and their levels. Since four control factors and three factor levels are considered, the $L_9(3^4)$ orthogonal array is employed to the study that requires nine experimental exercises, as shown in Table 2. In the present study, only the control factors will be analyzed. *The LZO precursor solution was*

Table 4 Inner array of the FWHM

Level	Cn (mol/kg)	Ratio of La(Ac)$_3$ to propionic acid	Heating rate (°C/min)	Annealing temperature (°C)	Average FWHM	*S*/*N* ratio
	Factor A	Factor B	Factor C	Factor D		
1	0.05	0.7	1	850	8.15	−18.23
2	0.05	1	5	900	11.68	−21.35
3	0.05	1.3	10	1,000	11.97	−21.56
4	0.08	0.7	5	1,000	8.84	−18.93
5	0.08	1	10	850	11.68	−21.35
6	0.08	1.3	1	900	7.33	−17.31
7	0.1	0.7	10	900	10.60	−20.51
8	0.1	1	1	1,000	10.51	−20.43
9	0.1	1.3	5	850	10.61	−20.52

Table 5 Response table of the FWHM

Level	Cn (mol/kg)	Ratio of La(Ac)$_3$ to propionic acid	Heating rate (°C/min)	Annealing temperature (°C)
	Factor A	Factor B	Factor C	Factor D
1 (Low)	−20.38	−19.22	−18.66	−20.03
2 (Medium)	−19.20	−21.04	−20.27	−19.72
3 (High)	−20.49	−19.80	−21.14	−20.31
S/*N* variation (maximum–minimum)	1.29	1.82	2.49	0.59
Contribution (%)	20.8	29.5	40.2	9.5
Ranking	3	2	1	4

relatively more stable than alkoxides in the air and the atmospheric ambient was kept constant in the laboratory. Other environmental factors, such as temperature or relative humidity are not incorporated in the analysis in this study as it is expected that they show minor effects.

2.2.3 Output response S/N in the Taguchi design

In the Taguchi method, effect of each experimental factor is examined by the variation of “response” by choosing an appropriate signal-to-noise (S/N) ratio. The S/N, which is defined as the ratio of signal power (the mean) to noise power corrupting the signal (the standard deviation), is an output response of a selected system and a measure for the robustness of the system. In general, three *S*/*N* equations are widely used: smaller-the-better response, larger-the-better response, and nominal-the-best response, as listed in Table 3 [17]. In the present study, the smaller-the-better and the larger-the-better equations are utilized to analyze the FWHM from XRD data and the surface integrity from FEGSEM images, respectively. The selected control variables are experimentally analyzed to determine how the coating process is likely to relate to “noise” which is uncontrollable, at appropriate factor levels to make the process less sensitive to variations in “noise factors”. In this way, the Taguchi method allows the process to be optimized.

3 Results and discussion

XRD patterns obtained by ω-scan for each practice of the Taguchi Design are shown in Fig. 2. The diffraction intensity from ω-scan reflects the degree of out-of-plane lattice alignment of LZO films. So the better the out-of-plane texture, the narrower the FWHM of the diffraction peak from ω-scan. Average FWHM values and *S*/*N* ratios from ω-scan diffraction peaks are obtained from three different samples synthesized in the same experiments, as summarized in Table 4. The average *S*/*N* values of the control factors at each level are shown in Table 5. A large variation in *S*/*N* ratios implies that the control factor has a great importance in the system. Among the control factors, the heating rate shows the largest fluctuation when varying the levels, indicating that it is the most important factor to determine the FWHM. A degree of importance for the factors in sequence is the heating rate, the ratio of the lanthanum acetate to the propionic acid, the precursor concentration used for inkjet printing, and the annealing temperature. Figure 3 schematically displays the control factors in the form of the response figures. It clearly shows that the optimum experimental conditions are 0.08 mol/kg for the precursor concentration, 0.7 for the ratio of the lanthanum acetate to the propionic acid, 1 °C/min for the heating rate, and 900 °C for the annealing temperature. The top two important values of the factors are 1 °C/min

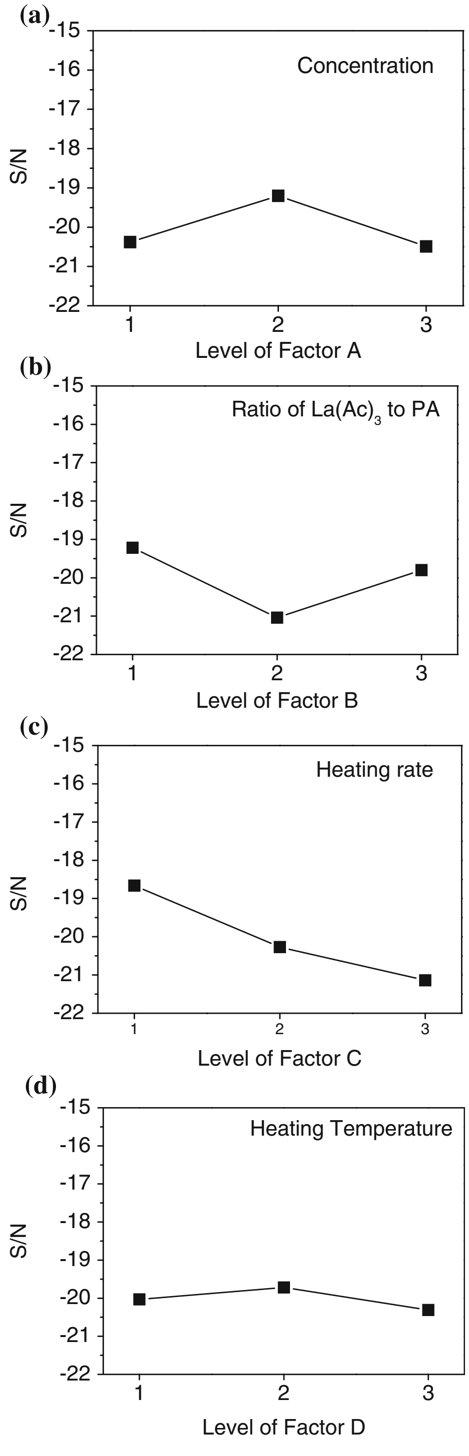

Fig. 3 Effect of concentration (**a**), ratio of lanthanum acetate to propionic acid (**b**), heating rare (**c**), and annealing temperature (**d**) on FWHM in the form of the response figure

heating rate and 0.7 ratio of lanthanum acetate to propionic acid. Figure 4 shows the change in the FWHM value relates to the heating rate for different ratios of lanthanum acetate to propionic acid (the annealing temperature and the concentration are not fixed). The FWHM grows with an increase in the heating rate regardless of the annealing temperature and concentration for any ratio of lanthanum acetate to propionic acid, implying the heating rate plays an important role. This elucidates the fact that the out-of-pane lattice alignment tends to be higher at a lower heating rate, which is ascribed to the fact that the LZO film has more time to undergo lattice arrangement. In addition, the FWHM value also changes as the ratio of lanthanum acetate to propionic acid varies, as shown in Fig. 4. This result implies that the solution chemistry has a great affect on the microstructures of the LZO films.

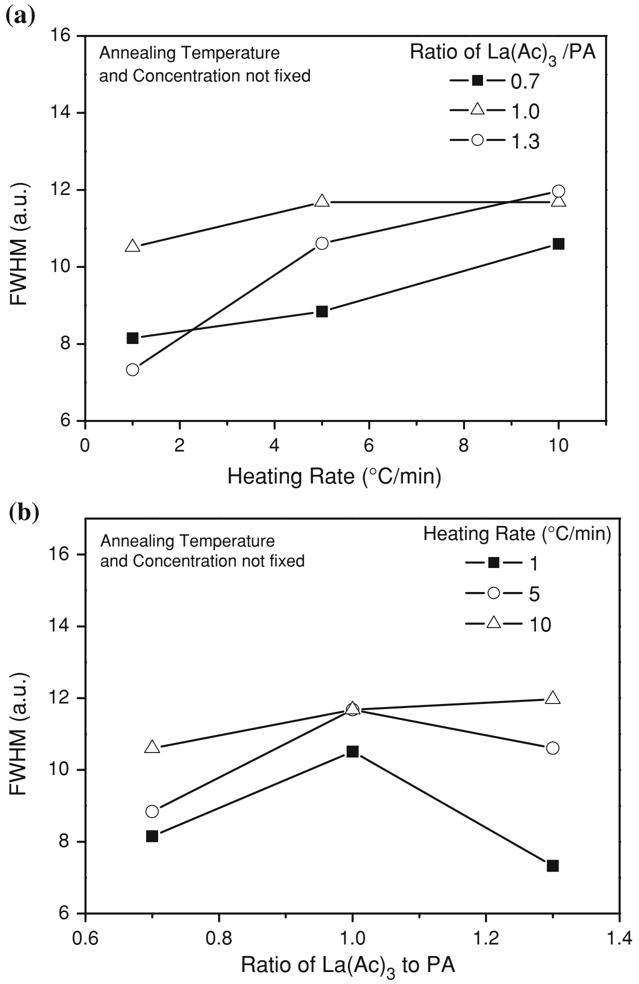

Fig. 4 FWHM values in relation to the heating rate for LZO films with different ratios of lanthanum acetate to propionic acid (**a**), and to the ratio of lanthanum acetate to propionic acid for LZO films with various heating rates (**b**). The annealing temperature and precursor concentration are not fixed

FEGSEM images of the LZO films of the Taguchi Design are shown in Fig. 5 (exercises 2, 4, 6 and 7). The *S*/*N* values, the response table, and the response figure of the surface integrity estimated from the FEGSEM images are shown in Tables 6, 7 and Fig. 6, respectively. The

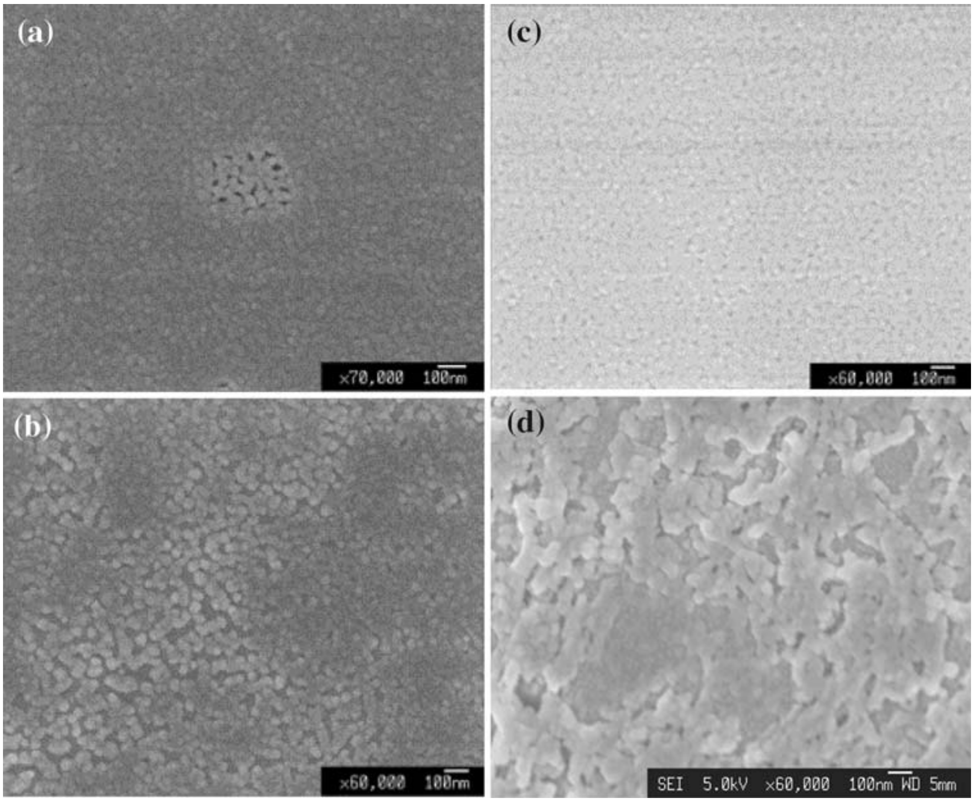

Fig. 5 FEGSEM images of the LZO film prepared using condition 2 (**a**), 4 (**b**), 6(**c**), 7(**d**) and in the Taguchi Design

Table 6 Inner array of the surface integrity

Level	Cn (mol/kg)	Ratio of $La(Ac)_3$ to propionic acid	Heating rate (°C/min)	Annealing temperature (°C)	Average surface integrity	*S*/*N* ratio
	Factor A	Factor B	Factor C	Factor D		
1	0.05	0.7	1	850	0.94	−0.57
2	0.05	1	5	900	0.98	−0.21
3	0.05	1.3	10	1,000	0.60	−4.63
4	0.08	0.7	5	1,000	0.91	−0.79
5	0.08	1	10	850	0.96	−0.32
6	0.08	1.3	1	900	0.97	−0.28
7	0.1	0.7	10	900	0.52	−6.07
8	0.1	1	1	1,000	0.85	−1.53
9	0.1	1.3	5	850	0.98	−0.22

Table 7 Response table of the surface integrity

Level	Cn (mol/kg)	Ratio of $La(Ac)_3$ to propionic acid	Heating rate (°C/min)	Annealing temperature (°C)
	Factor A	Factor B	Factor C	Factor D
1 (Low)	−1.80	−2.48	−0.80	−0.37
2 (Medium)	−0.46	−0.69	−0.40	−2.18
3 (High)	−2.61	−1.71	−3.67	−2.32
S/*N* variation (maximum–minimum)	2.15	1.79	3.27	1.95
Contribution (%)	23.5	19.5	35.7	21.3
Ranking	2	4	1	3

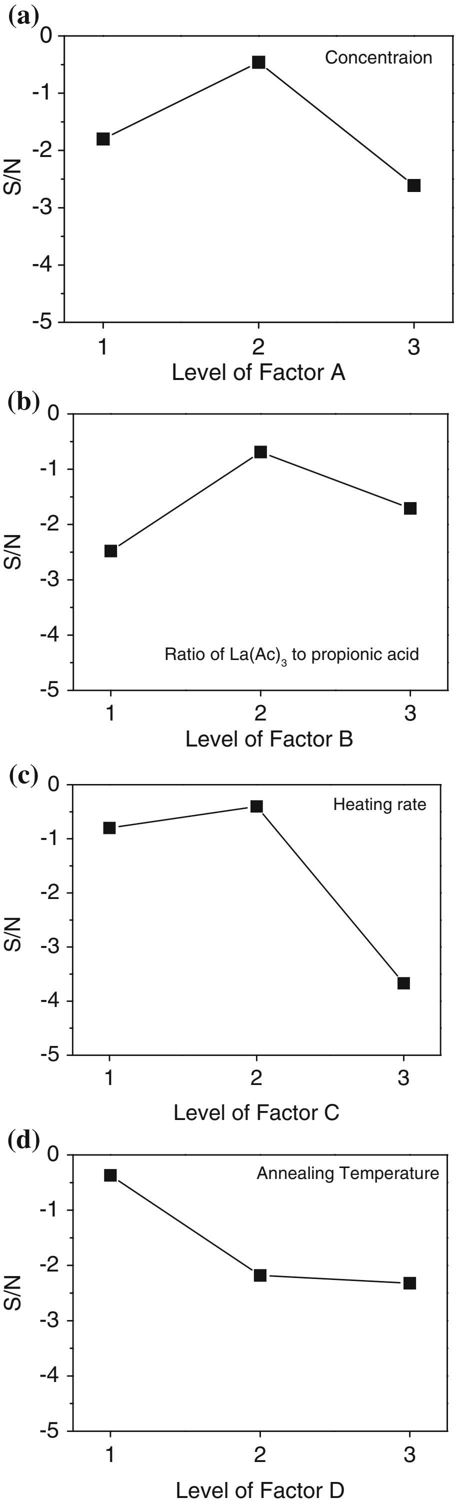

Fig. 6 Effect of concentration (**a**), ratio of lanthanum acetate to propionic acid (**b**), heating temperature (**c**), and annealing temperature (**d**) on surface integrity in the form of the response figure

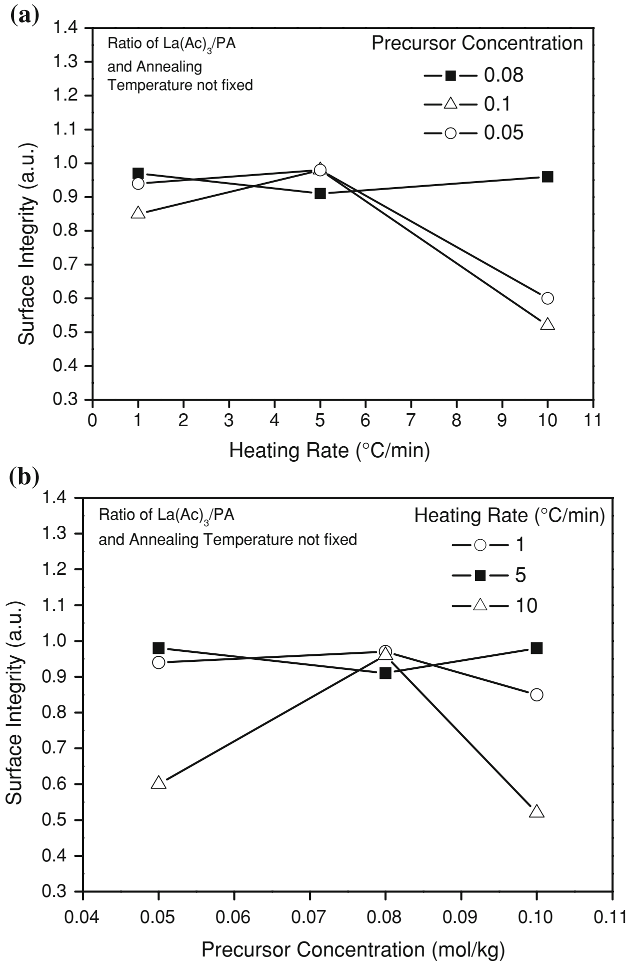

Fig. 7 Surface integrity values in relation to the heating rate for LZO film with various precursor concentrations (**a**), and to the precursor concentration for LZO film with different heating rates. The ratio of lanthanum acetate to propionic acid and the annealing temperature are not fixed

results indicate that the most important factor affecting the surface integrity is the heating rate, followed by the precursor concentration used for inkjet printing, the annealing temperature, and the ratio of lanthanum acetate in descending importance. The best values chosen are 0.08 mol/kg for the LZO precursor concentration, 1 for the ratio of lanthanum acetate to propionic acid, 5 °C/min for the heating rate, and 850 °C for the annealing temperature. Consequently, the first two important values of the factors are selected, i.e. the heating rate 5 °C/min and the precursor concentration 0.08 mol/kg. The influence of the surface integrity relating to the heating rate for LZO films with different precursor concentration and to the precursor concentration for LZO films with various heating rates (the annealing temperature and the annealing temperature not fixed) are shown in Fig. 7 (a) and (b), respectively. In general, the surface integrity values of the LZO films are satisfactory at lower heating rate and moderate precursor concentration.

On the basis of a comparison between the FWHM and the average surface integrity, a concentration of 0.08 mol/kg is suggested from both. The annealing temperatures of 900 and 850 °C are recommended by the FWHM and the surface integrity analyses, respectively. As shown in Tables 5 and 7, the relative contribution of the annealing temperature is 21.3% in the response table of the surface integrity, which is higher than 9.5% contribution from that of FWHM, thus 850 °C is chosen regarding optimizing of surface integrity. Similarly, for the ratio of lanthanum acetate to the propionic acid, 0.7 is selected with respect to the surface integrity as both the contribution and the ranking are higher than that in the FWHM in the response table of, as shown in Tables 5 and 7. For the heating rate, both 1 and 5 °C/min are recommended. While the statistical data show that the heating rate is the most important factor for both the FWHM and the surface integrity, 5 °C/min is picked with regard to FWHM. Based on the above analyses, the optimum experimental conditions chosen according to Taguchi design are: 0.7 for the ratio of the lanthanum acetate to the propionic acid, 0.08 mol/kg for the precursor concentration, and 850 °C for the annealing process using a heating temperature of 5 °C/min. Based on the experimental conditions, a LZO film has been prepared, as shown in Fig. 8. The film shows a dense structure according to the FEGSEM observation as shown in Fig. 8 (a) and possesses a high degree of out-of-plane alignment (FWHM ~7.9°), as shown in Fig. 8 (b).

In the present study, only 9 exercises are suggested by the Taguchi statistic method, which offers a shortcut solution to find suitable experimental conditions. However, it is not possible to obtain a clear comparison between every exercise due to a diversity of experimental conditions in each exercise. Nevertheless, by performing diverse experimental conditions, some useful information concerning the film formation is indeed discovered from our results. From FEGSEM images shown in Fig. 5, which correspond to Taguchi exercise #2, #4, and #7 respectively, they clearly show that the LZO films form by the coalescence of independent nanoparticles. Unlike Taguchi exercise #6, as shown in Fig. 5, the heating rates are faster in those exercises, so the nanoparticles could not form a denser film due to the limited time provided. Also, the results imply that the formation of the LZO films may be via inter-particles diffusion.

Finally, it has been shown that some carboxylate-related organics from the original precursors is present in LZO films in the annealing process [18]. This is consistent with the results given in Tables 5 and 7. The relative contribution to the FWHM and the surface integrity, of ratio of lanthanum acetate to propionic acid are 29.5 and 19.5%, respectively. This shows that carboxylate-related organics from precursors affect the formation of LZO films.

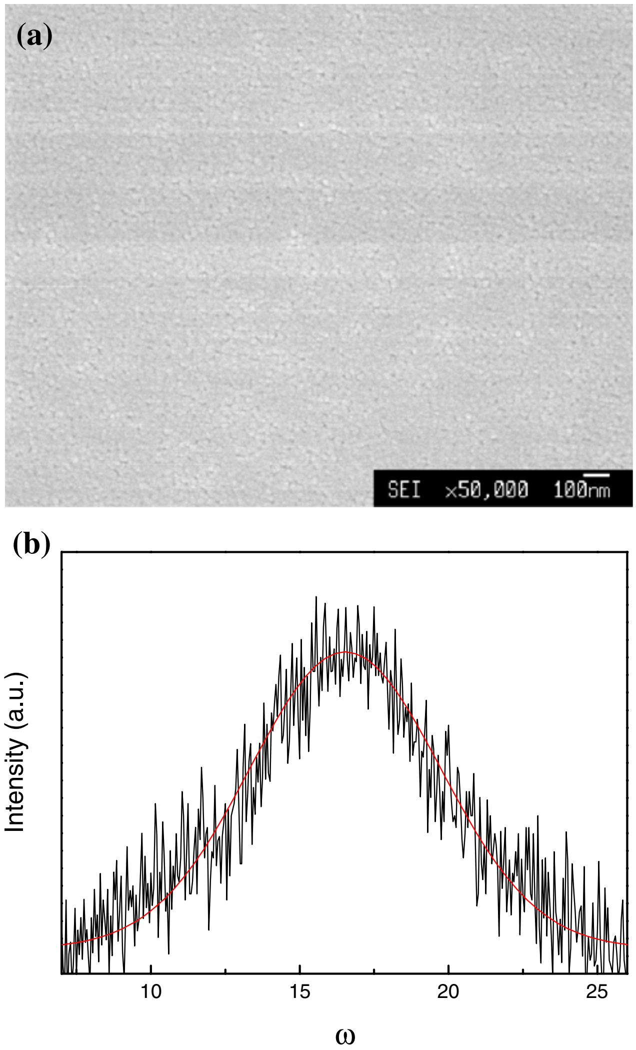

Fig. 8 **a** FEGSEM images of the LZO film prepared using the optimum condition suggested by the Taguchi Design. **b** XRD of the LZO film. Red line is simulated by Gaussian fitting

4 Conclusions

By considering the factors of LZO preparation process, four major parameters have been identified and used in the Taguchi statistical method: the ratio of lanthanum acetate to propionic acid, the concentration of precursor solution used in the inkjet printing system, the annealing temperature, and the heating rate. For the FWHM, a degree of importance for the parameters in sequence is the heating rate, the ratio of the lanthanum acetate to the propoionic acid, the precursor concentration used for inkjet printing, and the annealing temperature. On the other hand, for the average surface integrity, the most important factor is the heating rate, followed by the precursor concentration, the annealing temperature, and the ratio of lanthanum acetate in descending importance. The optimum experimental conditions as deduced from the Taguchi design are: 0.7 for the ratio of the lanthanum acetate to the propionic acid; 0.08 mol/kg for the precursor concentration; and 850 °C for the annealing process using 5 °C/min. The film synthesized using the optimum conditions reveals a dense surface morphology and high out-of-plane lattice alignment. This work has shown that the Taguchi method is a viable approach for "picking good experimental conditions" for achieving excellent quality LZO film by ink-jet printing from a selected precursor solution.

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