JOURNAL OF MATERIALS SCIENCE **37** (2002) 1337–1342

Optimization of the experimental conditions for the preparation of a thin strontium titanate film by hydrothermal process

WEIN-DUO YANG*
Department of Chemical Engineering, National Kaohsiung University of Applied Sciences, Kaohsiung 80807, Taiwan; Materials Science 138-78, California Institute of Technology, Pasadena, CA 91125, USA
E-mail: ywd@caltech.edu

KUN-MING HUNG
Department of Chemical Engineering, National Kaohsiung University of Applied Sciences, Kaohsiung 80807, Taiwan

A Taguchi orthogonal array design was implemented to optimize the experimental conditions for the preparation of a thin strontium titanate film on a Ti substrate using a hydrothermal process. The effects of such preparatory conditions as the strontium-concentration, pH-value, reaction temperature, reaction time and the substrate surface treatment were systematically studied. Results indicate that the effects of the reaction temperature and reaction time are the key variables influencing the relative crystal intensity (intensity of (110) $SrTiO_3$ peaks in XRD spectrum/intensity of (101) Ti peak in XRD spectrum) of the films obtained. By combining the optimal settings of the two most influential process variables, a polycrystalline, $SrTiO_3$-films was obtained, with improved crystallinity and a grain size of 0.2–0.4 μm and a dielectric constant of 360 at I MHz.

1. Introduction

The semiconductive and dielectric properties of perovskite ceramics such as $SrTiO_3$, $BaTiO_3$ and $CaTiO_3$ are widely applied in electronic components, such as photoelectrodes [1, 2], devices of various boundary-layer capacitors [3, 4] and humidity sensors [5]. For the development of VLSI circuits, it is necessary to coat a substrate with a thin film of a material with a high dielectric constant [6, 7].

Strontium titanate film has a high dielectric constant and is used in the manufacturing of dynamic random access memory chips (DRAM) [8]. It is of great importance to prepare very thin films on the substrate. The grain size, dielectric constant and the chemical reactions taking place at the boundary of the coating film and the substrate are also important and have to be taken into consideration.

There are various methods for manufacturing thin films, for example physical vacuum deposition [9], ion beam sputtering [10], electron beam evaporation [11], and pulsed laser ablation [12]. In recent years, however, chemical methods for the deposition of thin films found broader application and substitute more and more physical methods. Chemical methods include sol-gel techniques [13, 14], metallo-organic decomposition (MOD) [15], and chemical vapor deposition (CVD) [16, 17]. Temperatures used in the application of chemical processes are usually lower (400–800°C) than the ones used in physical methods. Another advantage is that large area films can be produced without necessitating an extra high vacuum environment. A disadvantage though is that cracking in the films has been observed during the heat treatment process. Yoshimura *et al.* [18] discovered that a thin $BaTiO_3$ film on a Ti substrate can be produced by an electrochemical process, using a titanium cathode in an alkaline Ba^{2+} solution. Further studies, however, showed that electrolysis was unnecessary, and a $BaTiO_3$ film could also be produced in a hydrothermal bath. Using Sr^{2+} instead of Ba^{2+}, a fine $SrTiO_3$ film can also be obtained [19, 20].

Fractional factorial design is a reliable method for simplifying the process of identifying the most influential preparation variables. It reduces the number of experiments required to identify the critical process variables in a statistically significant fashion [21, 22]. Until now, to the best of our knowledge, the literature does not contain any reports that investigate the optimization of experimental conditions in the preparation of $BaTiO_3$ films by a hydrothermal process.

In this study, we used the hydrothermal method to prepare a strontium titanate thin film on a Ti substrate. Taguchi's orthogonal array [23, 24] was employed in planning experiments that study the effects of such preparation variables as the Sr^{2+} concentration of the

---

*Author to whom all correspondence should be addressed.

solution, pH-value, reaction temperature, reaction time and the substrate surface treatment on the grain size of the film, and to determine which experimental parameter settings affect the grain size and dielectric constant of the film. The relative crystal intensity (intensity of (110) $SrTiO_3$ peaks in XRD spectrum/intensity of (101) Ti peak in XRD spectrum) was chosen as another parameter to evaluate the character of the produced films. Optimal preparatory conditions could be singled out and a film with a high dielectric constant was prepared under those conditions.

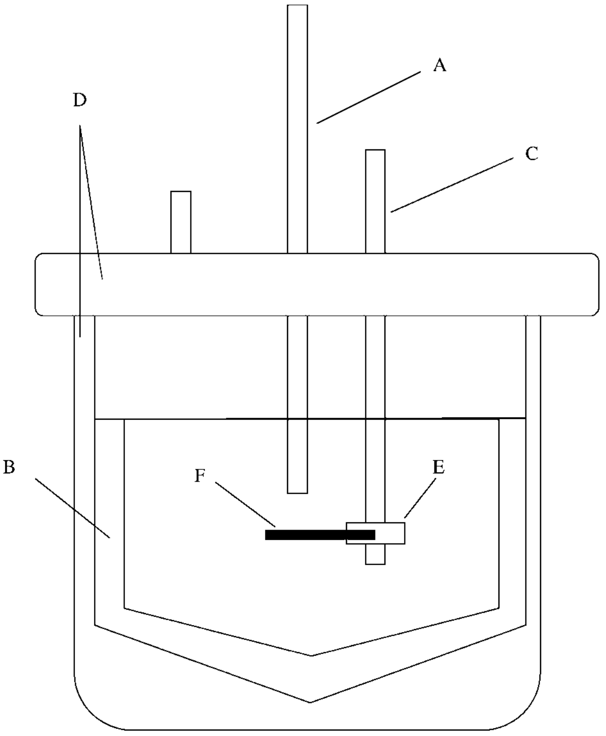
2. Experimental procedure

2.1. Synthesis of a thin strontium titanate film

Strontium titanate films were prepared on titanium substrates by a hydrothermal method using an aqueous solution of $Sr(OH)_2$. The solution was prepared with boiling deionized water in order to remove dissolved CO_2 that could produce insoluble strontium carbonate. The solution was placed in a teflon beaker inside an autoclave as shown in Fig. 1. The films were fabricated by putting a 1 mm thick titanium substrate in the solution under hydrothermal conditions.

2.2. Fractional factorial design

Taguchi's orthogonal array table was implemented by choosing five primary process variables that could affect the characteristics of the films, namely: (A) concentration of Sr^{2+}, (B) pH-value, (C) reaction temperature, (D) reaction time, and (E) surface treatment (polishing) of the Ti substrate (see Table I).



A: thermocouple
B: teflon beaker
C: stainless stell baar
D: stainless steel reactor
E: Teflon clamp
F: Ti-substrate

Figure 1 Schematic illustration of the preparation of thin strontium titanate films by hydrothermal process.

TABLE I Factors and levels for the fractional factorial design

	Levels	
Factors	High (2)	Low (1)
A Sr^{2+}-concentration (M)	4	0.5
B pH-value (room temperature)	>13	11–12
A × B Consider the interaction of A and B		
C Reaction temperature (°C)	200	130
D Reaction time (hr)	20	3
E Surface treatment	polished	unpolished

TABLE II The design matrix and experimental data of the Taguchi orthogonal array

	A	B	A × B	C	D	E	Error	Relative crystal intensity (×1000)
1	1	1	1	1	1	1	1	50
2	1	1	1	2	2	2	2	300
3	1	2	2	1	1	2	2	80
4	1	2	2	2	2	1	1	310
5	2	1	2	1	2	1	2	200
6	2	1	2	2	1	2	1	260
7	2	2	1	1	2	2	1	120
8	2	2	1	2	1	1	2	240

If each of these variables were assigned two values, a low and a high one, and a factorial experimental design were employed using each of these values, the number of permutations would be 2^5, meaning that 32 experiments are required to identify the optimal setting of the experimental variables. However, the fractional factorial design approach we used reduced the number of necessary experiments to eight, while maximizing the amount of information derived from this reduced set of experiments [25]. The structure of the experimental sets using Taguchi's orthogonal array is shown in Table II.

2.3. Testing methods

Scanning electron microscopy (SEM) was used to analyze the microstructures of the films. X-ray diffraction (XRD) was used to characterize the perovskite phases of the films.

The phases of the films were examined using an X-ray diffraction analyzer. SEM was used to characterize their surfaces. The dielectric constants of the films were measured with an HP impedance analyzer 4284 A.

3. Results and discussion

3.1. Preparation of strontium titanate film by hydrothermal process

In the study we used the reaction of Sr^{2+} with Ti metal to obtain a strontium titanate film on a Ti-substrate in a strong alkaline solution. The reaction variables (A) concentration of Sr^{2+}, (B) pH-value, (C) reaction temperature, (D) reaction time, and (E) surface treatment have been investigated for their effects on the relative crystal intensity of $SrTiO_3$ to Ti, and on the dielectric constants of the resulting thin ceramic films.

Xu *et al.* produced a $BaTiO_3$ film by putting a Ti metal substrate into a strongly alkaline solution of Ba^{2+} [26]. The alkali earth ions diffuse into the substrate surface, where $BaTiO_3$ is formed. In our studies, two

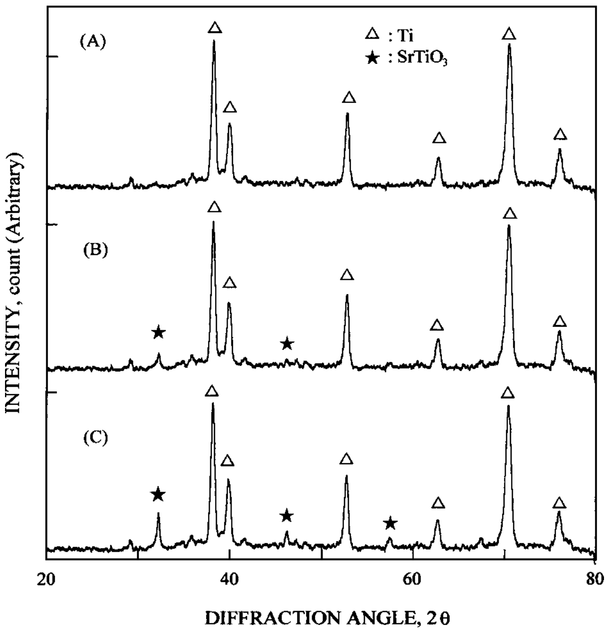


Figure 2 The XRD patterns of the thin films. (A) the film prepared at $[Sr^{2+}] = 4$ M, reaction time = 3 hrs, reaction temperature = 120°C; (B) $SrTiO_3$ film prepared at $[Sr^{2+}] = 4$ M, reaction time = 3 hrs, reaction temperature = 130°C, and (C) $SrTiO_3$ film prepared at $[Sr^{2+}] = 0.5$ M, reaction time = 3 hrs, reaction temperature = 200°C.

$Sr(OH)_2$ solution with different pH-values were used. The one with the lower pH-value (pH ≅ 11 at room temperature) was produced by dissolving only $Sr(OH)_2$ in water, the one with the higher pH-value (pH ≅ 13 at room temperature) was produced by adding NaOH to the $Sr(OH)_2$ solution. Results show that the stronger alkaline solution produced a $SrTiO_3$ film with a finer grain size.

The results of the investigation of the reaction temperature influence on the film formation indicate that a higher reaction temperature (200°C) leads to a stronger crystal intensity, and a larger grain size of the film (about 0.6–0.8 μm). A lower reaction temperature (130°C) produces a smaller grain size (about 0.1–0.2 μm). These results suggest a proportional relationship between the relative crystal intensity of the obtained film and the reaction temperature. The relative crystal intensity of the film is stronger for a higher reaction temperature and the dielectric constant of the film formed at that temperature is also higher.

A $SrTiO_3$-film could not be produced at reaction temperature below 130°C, even at a high concentration of Sr^{2+} (4 M). Fig. 2A shows the XRD pattern of the Ti metal substrate subjected to those conditions; no $SrTiO_3$ was detected. Fig. 2B shows the XRD pattern of the $SrTiO_3$ film obtained at 130°C. The XRD pattern of the $SrTiO_3$ film produced at 200°C by subjecting the Ti substrate for 3 hrs to a 0.5 M Sr^{2+} solution is shown in Fig. 2C. The relative crystal intensities of the $SrTiO_3$ films vary with the reaction temperature. Films produced at a higher reaction temperature show a stronger relative crystal intensity.

In all the experiments we carried out the minimum setting for the reaction time was 3 hrs, for the reaction temperature 130°C, and for the Sr^{2+} concentration 0.5 M, in order to obtain a film. The reaction time influenced the crystal growth and grain size. With an increase in the relative crystal intensity increased as well. However, using very long reaction times (i.e. 30 hrs) produced a film with an inhomogeneous distribution of grains and a tendency for aggregation was observed. Concomitantly, the relative crystal intensity decreased as well.

An increase in pH-value was achieved by adding a 0.5 M NaOH solution to the Sr^{2+} solution (pH >13 at room temperature). At the higher pH-value, the film was more homogeneous. In a trial experiment at pH >13, a reaction temperature of 200°C, and a reaction time of 20 hrs, the obtained $SrTiO_3$ film still had a weak relative crystal intensity, but the film thickness was not visibly affected. The mechanism of formation of titanate film could be explained by Xu that at a high OH^- concentration there is a tendency for highly densified and fine $Ti(OH)_4$ to form on the Ti substrate surface [26]. Only small pores exist, which make it difficult for the alkali earth metal ion to diffuse into the bulk of $Ti(OH)_4$. As a result, the produced titanate film is very thin.

In another experiment the substrate was polished with a diamond grinder paste (1000 μm) to produce a smooth surface. The $SrTiO_3$ film on this smooth surface was, under the SEM, visibly more homogeneous than the $SrTiO_3$ produced on an unpolished surface. During the reaction of Sr^{2+} with a Ti-substrate in a strong alkaline solution, a $Ti(OH)_4$gel is formed as a first step [27]. Then the Sr^{2+} ions diffuse into the surface of the titanium gel film to form $SrTiO_3$. This diffusion process is controlled by the morphology of the titanium gel [28]. Therefore, the shape and size of the precursor gel have a strong influence on the properties and composition of the final film. In our experiment, the $Ti(OH)_4$ gel film that formed on the surface of the unpolished Ti-substrate was inhomogeneous due to the coarseness of the surface and the resulting $SrTiO_3$ film in turn was coarse too.

A change in the preparatory variables of the experiment affects indirectly the formation of the $Ti(OH)_4$ gel, changes the mole of the nucleophilic attack of the Sr^{2+} on the titanium-gel, and can even control the grain growth and relative crystal intensity of the produced powder. (In our experiments, the chosen preparatory conditions for the formation of a strontium titanate film were reaction temperatures of either 130°C or 200°C, a reaction time of 3 hrs or 20 hrs, and a Sr^{2+}-concentration of 0.5 M or 4 M.) The compositions of the $SrTiO_3$ films were uniform, and the relative crystal intensities were about 0.1–0.3, grain sizes were 0.2–0.6 μm, film thickness was 0.1–0.6 μm and dielectric constants were 150–350.

3.2. Experimental design

3.2.1. *Taguchi array design*

A Taguchi orthogonal array design was used to identify the optimal preparatory conditions and to single out the factors having the most profound influence on the relative crystal intensity of the $SrTiO_3$ (110) plane to the Ti (101) plane of the thin $SrTiO_3$ film. The preparatory conditions investigated were (A) Sr^{2+}concentration, (B) pH-value, (A × B) possible interaction of Sr^{2+}-concentration and pH, (C) reaction temperature, (D) reaction time and (E) Ti-substrate surface treatment. In previous experiments the above factors have all been proven to have an effect on the relative crystal intensity of the $SrTiO_3$ film.

In our study, a 2-level Taguchi array $L_8(2^7)$ [29], was used to describe the experiments. 8 indicates the number of experiments performed, 2 describes the two different setting (levels), high or low, of the investigated variables and 7 is the number of different variables (different factors) taken into account. The low level (represented by 1) and high level (represented by 2) of the preparatory factors are shown in Table I. The experimental conditions and results of the experiments are given in Table II. In the table, columns 1 to 7 represent the experimental conditions, and column 8 shows the relative crystal intensity of $SrTiO_3$ to Ti obtained in each run. The films were characterized by XRD to detect perovskite phases. The relative crystal intensity, the grain sizes, film thickness and dielectric constants were also determined.

3.2.1.1. Analysis of variance. The variance of the relative crystal intensity in Table II was computed to identify the most influencial preporatory, factors: results are shown in Table III (Analysis of Variance). In the table, S_i represents the sum of square of column i and was computed according to the following equation:

$$S_i = \left(\Sigma x_i^{\text{low level}} - \Sigma x_i^{\text{high level}}\right)^2 \Big/ n_t \qquad (1)$$

where n_t total number of experiments (= 8 in our case) and $x_i =$ relative crystal intensity.

For factor A (Sr^{2+}-concentration), for example, S_A is calculated as:

$$S_A = [(50 + 300 + 80 + 310) - (200 + 260 + 120 + 240)]^2/8 = 800 \qquad (1A)$$

S_T in Table III is the total sum of squares and was calculated using

$$S_T = \Sigma S_i \qquad (2)$$

V_i represents the mean square (or unbiased variance) of factor i. It was computed using the following equation:

$$V_i = S_i/\phi_i \qquad (3)$$

ϕ_i is the degree of freedom.

The next step was to calculate the distribution F_i:

$$F_i = V_i/V_e \qquad (4)$$

V_e is the mean square of the 7th "error" factor.

As seen in Table III, the calculated values for $F_{A\times B}$, F_C and F_D are substantially higher than F_A, F_B and F_E. High values for the calculated distribution F_i mean a greater influence of factor i on the experimental outcome. The highest F_i values were calculated for F_C (factor: reaction temperature) and F_D (factor: reaction time). These two factors seem to be the most influental ones. At 5% significance (0.05) the identification value F (1, 1, 0.05) is 161, at 1% significance (0.01) the identification value F (1, 1, 0.01) is 4052 [30]. We set 5% significance (0.05) as our identification value F. Our calculated F_i-values are all significantly lower than the identification value F, implying that none of the investigated factors has a significant influence on the result of the experiment. That could be explained by the fact that the degree of freedom of error is too small to affect the accuracy of identification.

TABLE III Table of analysis of variance

	Sum of square (S_i)	Degree of freedom (ϕ_i)	Mean square (V_i)	Distribution (F_i)
A	800	1	800	1.00
B	450	1	450	0.56
A × B	2450	1	2450	3.06
C	54450	1	54450	68.06
D	11250	1	11250	14.06
E	200	1	200	0.25
Error	800	1	800	–
S_T	70400	–		–

3.2.2. The pooling method

Using an orthogonal array, the results of the experiments have a small degree of freedom and therefore a pooling method is used to increase the freedom of error ϕ_e. The three lowest S_i values were combined (summation) with the error term. In the analysis of variance (Table III) the F_i values of factors A, B and E were 1.00, 0.56 and 0.25, all significantly lower than $F_{A\times B}$, F_C and F_D. This indicates that factors A (Sr^{2+}-concentration), B (pH-value) and E (surface treatment) have a lesser effect on the relative crystal intensity of the obtained $SrTiO_3$ film. Therefore, the three factors were combined ("pooled") with the error term. The analysis of error variance is shown in Table IV. In Table IV, after combining S_A, S_B and S_E with S_e, the degree of freedom of error is $\phi_e = 4$.

After recalculating the values in the analysis of error variance, the F_C-value (reaction temperature) and F_F-value (reaction time) are 96.8 and 20.0, respectively. Both F-values are larger than the identification value $F(1, 4, 0.05) = 7.71$ [30]. $F_{A\times B}$ (interaction of Sr^{2+}-concentration and pH-value) is still lower than the identification value F. Therefore, the Sr^{2+}-concentration has no significant effect on the obtained relative crystal intensity. The reaction temperature and reaction time

TABLE IV The analysis of variance for the pooling method

	Sum of square (S_i)	Degree of freedom (ϕ_i)	Mean square (V_i)	Distribution (F_i)
A × B	2450	1	2450	4.4
C	54450	1	54450	96.8
D	11250	1	11250	20.0
Error	2250	4	562.5	–
S_T	70400	–	–	–

TABLE V The grain size, film thickness and dielectric constant of films prepared in Table I

Sample	Run 1	Run 2	Run 3	Run 4	Run 5	Run 6	Run 7	Run 8
Grain size (μm)	0.1–0.2	0.2–0.4	0.1–0.2	0.2–0.4	0.1–0.3	0.3–0.6	0.1–0.3	0.2–0.4
Film thickness (μm)	0.1–0.3	0.4–0.6	0.2–0.4	0.4–0.6	0.3–0.5	0.3–0.6	0.2–0.4	0.3–0.5
Dielectric constant (at 1 MHz)	210	315	230	330	265	305	245	285

were identified as the most influential factors in preparing a high crystal $SrTiO_3$ film.

3.2.3. The relationship between relative crystal intensity, grain size, film thickness and dielectric constant

The grain size, film thickness and dielectric constant of the films prepared are shown in Table V. The table indicates that both the grain size and dielectric constant are proporational to the relative crystal intensity, i.e. a higher relative crystal intensity results in a higher dielectric constant.

A different relationship exists between the film thickness and the relative crystal intensity. For shorter reaction times (3 hrs) the film thickness increased as the relative crystal intensity and the dielectric constant increased. However, at long reaction times (20 hrs) the film thickness continued to increase, whereas the dielectric constant and relative crystal intensity decreased. In a further calculation we chose the dielectric constant (insteaded) of the relative crystal intensity) as the objective criterion to determine the most influential factors, and implemented the Taguchi orthogonal array design. The results proved again that the reaction temperature and reaction time were the most important factors influencing the dielectric constant of the obtained $SrTiO_3$ polycrystal thin film.

3.3. Optimal conditions and control experiment

The average relative crystal intensities, with the reaction temperature set at low level and high level, are 0.113 and 0.278, respectively. The average relative crystal intensities obtained when the reaction time was set at low level and high level are also 0.158 and 0.233. The optimal preparatory conditions can be combined as C_2D_2 (both reaction temperature and reaction time are at high level). The relative crystal intensity of the resulting $SrTiO_3$ film to Ti substrate is theoretically given as:

$$\begin{aligned}\mu(C_2D_2) &= \mu(C_2) + \mu(D_2) - \mu\\ &= 0.278 + 0.233 - 0.195 = 0.316\end{aligned}$$

where $\mu(C_2D_2)$ optimal relative crystal intensity, $\mu(C_2)$ relative crystal intensity at high-level of reaction temperature, $\mu(D_2)$ relative crystal intensity at high-level of reaction time, and μ the average relative crystal intensity of total number of experiments.

This theory was confirmed in a control experiment. In this experiment the Sr^{2+} concentration of the solution was set at 0.5 M, pH-value was 13–14, reaction temperature was 200°C, reaction time was 20 hrs and the substrate surface was polished with 1 μm diamond paste. A crystal $SrTiO_3$ film was obtained with properties described below.

3.4. Comparison of two representative films from the eight test runs with the film obtained in the control experiment

The XRD patterns of some of the obtained films are shown in Fig. 3. Fig. 3A is the film prepared from run 1 in Table II, having a relative crystal intensity of 0.05

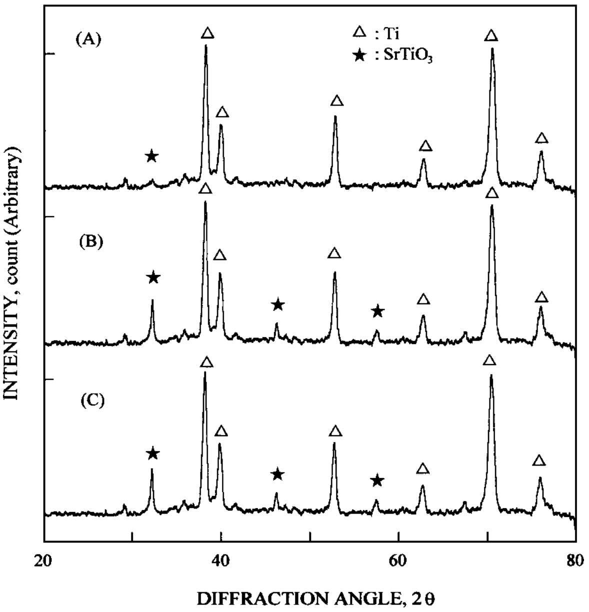


Figure 3 The XRD patterns of the obtained films. (A) the film prepared from run 1 in Table II; (B) the film prepared from run 4 in Table II, and (C) the film from the control experiment with a relative crystal intensity of about 0.32.

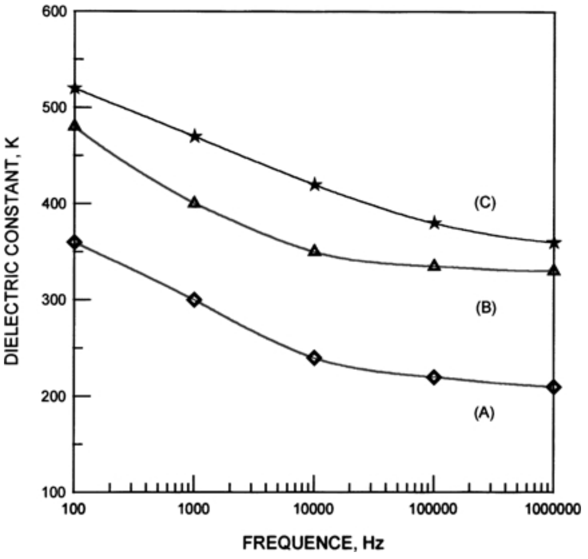


Figure 4 Dielectric constant of $SrTiO_3$ films. (A) the film of run 1 in Table II; (B) the film of run 4 in Table II (C) the confirmation experiment film.

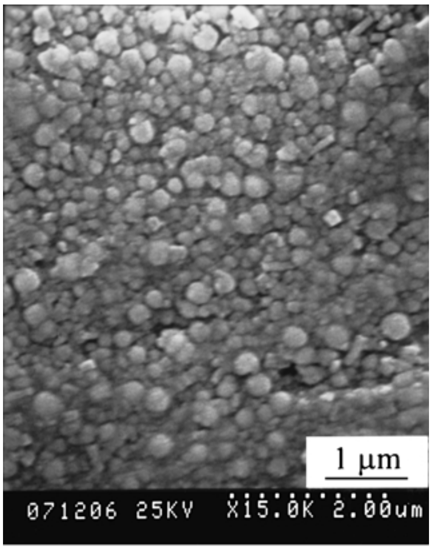


Figure 5 SEM micrographs of the strontium titanate film prepared by the confirmation experiment.

(intensity of (110) $SrTiO_3$ peaks in XRD spectrum/intensity of (101) Ti peak in XRD spectrum). Fig. 3B is the film from run 4, having a relative crystal intensity of 0.31. Fig. 3C shows the film from the control experiment with a relative crystal intensity of about 0.32.

The dielectric constants of the films obtained from run 1, run 4, and the control experiment were measured at various frequencies. Results are shown in Fig. 4. Obviously, a higher relative crystal intensity results in a higher dielectric constant. The dielectric constant of the film obtained in the control experiment was 360 at 1 MHz. Fig. 5 shows that the film has a grain size of 0.2–0.4 μm.

4. Conclusions

Polycrystal strontium titanate films were obtained from strontium hydroxide in a hydrothermal reaction with a Ti substrate. The effects of such preparatory conditions as the Sr^{2+} concentration of the solution, pH-value, reaction temperature, reaction time and the substrate surface treatment were systematically studied using Taguchi's orthogonal array design. Results indicate that reaction temperature and reaction time are the key variables influencing the relative crystal intensity and dielectric constants of films obtained. By combining the optimal settings of these two influential process variables, a polycrystalline $SrTiO_3$-film with a high dielectric constant could be obtained.

Acknowledgements

The author thanks the National Science Council, NSC 89-2214-E-151-004, for the financial support of this work.

References

1. R. WU and W. A. SCHULZE, *J. Amer. Ceram. Soc.* **75** (1992) 3390.
2. B. T. CHANG, *Solid State Comm.* **43** (1982) 335.
3. G. ARIT and D. HENNINGS, *J. Appl. Phys.* **58** (1985) 1619.
4. C. F. KAO and W. D. YANG, *Mater. Transaction JIM* **37** (1996) 142.
5. Y. C. YEH and T. Y. TSENG, *J. Mater. Sci. Lett.* **7** (1988) 766.
6. Y. NAKANO, M. WATANABE and T. TAKAHASHI, *J. App. Phys.* **70** (1991) 1539.
7. D. ROY, C. J. PENG and S. B. KRUPANIDHI, *Appl. Phys. Lett.* **60** (1992) 2478.
8. T. SAKUMA, S. YAMAMICHI, S. MATSUBARA, H. YAMAGUCHI and Y. MIYASAKA, *ibid.* **57** (1990) 2431.
9. W. B. PENNEBAKER, *IBM J. Res. Dev.* **13** (1985) 686.
10. S. YAMAMICHI, T. SAKUMA, K. TAKEMURA and Y. MIYASAKA, *Jpn. J. Appl. Phys.* **30** (1991) 2193.
11. H. MORI and H. ISHIWARA, *ibid.* **30** (1991) L1415.
12. T. HIRANO, T. FUJI, K. FUJINO, K. SAKUTA and T. KOBAYASHI, *ibid.* **31** (1992) L511.
13. F. M. PONTES, E. J. H. LEE, E. R. LEITE, E. LONGO and J. A. VARELA, *J. Mater. Sci.* **35** (2000) 4783.
14. P. C. JOSHI and S. B. KRUPANIDHI, *Appl. Phys. Lett.* **61** (1992) 1525.
15. J. V. MANTESE, A. L. MICHELI, A. H. HAMDI and R. W. VEST, *MRS Bull.* **10** (1989) 48.
16. G. BRAUNSTEIN and G. R. PAZ-PUJALT, *Thin Solid Films* **216** (1992) 1.
17. W. A. FEIL, B. W. WESSELS, L. M. TONGE and T. J. MARKS, *J. Appl. Phys.* **67** (1990) 3858.
18. M. YOSHIMURA, S. E. YOO, M. HAYASHI and N. ISHIZAWA, *Jpn. J. Appl. Phys.* **28** (1989) L2007.
19. S. E. YOO, M. HAYASHI, N. ISHIZAWA and M. YOSHIMURA, *J. Amer. Ceram. Soc.* **73** (1990) 2561.
20. N. ISHIZAWA, H. BANNO, M. HAYASHI, S. E. YOO and M. YOSHIMURA, *Jpn. J. Appl. Phys.* **29** (1990) 2467.
21. G. E. P. BOX, W. G. HUNTER and J. S. HUNTER, "Statistics for Experimenters An Introduction to Design, Data Analysis, and Model Building" (Wiley, New York, 1978) p. 510.
22. C. H. YANG, S. M. LIN and T. C. WEN, *Polymer. Eng. and Sci.* **36** (1994) 146.
23. M. W. WEISER and K. B. FONG, *Amer. Ceram. Bull.* **72** (1993) 87.
24. W. D. YANG and C. S. HSIEH, *J. Mater. Res.* **14** (1999) 3410.
25. TAGUCHI and GENICHI, "System of Experimental Design," Vol. 1 and 2 (UNIPUB, New York and American Supplier Institute, Dearborn, MI, 1988).
26. M. WU, R. XU and S. H. FENG, *J. Mater. Sci.* **31** (1996) 6201.
27. M. I. DIAZ-GUEMES, T. G. CARRENO and C. J. SERNA, *ibid.* **24** (1989) 1011.
28. C. F. KAO and W. D. YANG, *Material Science and Engineering* **B38** (1996) 127.
29. P. J. ROSE, "Taguchi Techniques for Quality Engineering," 2nd ed. (McGraw-Hill, New York, 1996) p. 75.
30. G. E. P. BOX, W. G. HUNTER and J. S. HUNTER, "Statistics for Experimenters: An Introduction to Design, Data Analysis, and Model Building" (Wiley, New York, 1978), p. 630.

Received 10 April
and accepted 11 December 2001