

Deposition of $\text{Ba}_{1-x}\text{Ca}_x\text{Ti}_{1-y}\text{Zr}_y\text{O}_3$ Films on HR-Si Substrate Using RF Sputtering by Design of Experiment Method

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Abstract

In this paper, the optimization compositions of $\text{Ba}_{1-x}\text{Ca}_x\text{Ti}_{1-y}\text{Zr}_y\text{O}_3$ (BCZT) films doping yttrium were obtained characteristic of low loss and high dielectric constant using design of experiment (DOE) method at microwave frequency region. The BCZT films were physical deposited using RF magnetron sputtering system on LaNiO_3 (LNO)/Au/Ti/SiO₂/HR-Si substrate which is MIM structure. The LaNiO_3 buffer layer was enhanced (100) direction growth of the BCTZ films, and high resistivity silicon was used to inhibit substrate loss. Design the $\text{Ba}_{1-x}\text{Ca}_x\text{Ti}_{1-y}\text{Zr}_y\text{O}_3$ mole fraction range between $x = 0\sim 0.1$ and $y = 0.1\sim 0.25$, were discussed the different compositions of Ca and Zr to influence the electrical properties of the films and measured the microwave characteristic using circular-path capacitor structure and a loss corrected model. The ferroelectric films conditions as adding 10 mol% Ca, 25mol% Zr, and Y doping 3 at% at deposited temperature at 600°C, the excellence dielectric properties which dielectric constant is 91 and lowest dielectric loss is 0.055 were appeared at 2.45GHz. The film crystal structures were determined using the X-ray diffraction (XRD) and the microstructure were obtained using field-emission scanning electron microscopy (FE-SEM). The microwave dielectric properties were investigated by Agilent E8364A network analyzer with probe station.

Key words: Ferroelectric, Design of Experiment, Buffer layer, Microwave

Introduction

High dielectric performance of ferroelectric materials has received considerable attention due to their feasibility in microwave devices applications. The barium zirconium titanate-based (BZT-based) or barium strontium titanate (BST) thin films are largely used source of the excellent characteristic such as high dielectric constant and low leakage current. The ferroelectric phase transition at the Curie point (T_c) of BZT materials is well-known to change strongly with the zirconium content. [1, 2] As the zirconium content increases, these materials show diffuse ferroelectric phase transitions, which are characterized by broadened dielectric maxima at T_c . The broadening of the dielectric maximum has been attributed to a distribution of Curie points, which is caused by inhomogeneous distribution of Zr ions on B-sites and mechanical stress in the grains. In the related system of $\text{Ba}_{1-x}\text{Ca}_x\text{Ti}_{1-y}\text{Zr}_y\text{O}_3$ (BCZT), the dielectric constant of BCTZ is significantly higher than BZT or BST. [3] Doping Ca ions not only are substituted for Ba ions

but also find other sites in the crystal lattice, which Ca ions replaces the sites of Ti ions to catch free electrons for reducing tangent loss. [4] The researchers also doped Rare-earth elements, as Y ions, to dissolve in both the A-sites and B-sites depending on the A/B ratio in BaTiO_3 system. Y acts as a donor and compensates for oxygen vacancies caused by acceptors which are added for enhancing non-reducibility. [5] Any descriptions on fabrication and on dielectric properties of BCTZ thin films at microwave frequency have less discussion in the literature. Therefore, selecting an acceptable condition and composition range is necessary to perform study. Single-variable experiment is the most familiar and effective method to characterize each parameter effect on the thin film properties. Nevertheless, it is also less studies for more effective and reasonable approach to search the optimum conduction of the system. The design of experiment (DOE) method is a powerful technique to optimize a complicated process. Using the DOE method, the tool may find out the interaction of factors and obtain the optimize conditions

associated with specific properties by fewer experiments than the traditional single-variable or try-and-error method. [6]

In this study, we reported the optimization compositions of $\text{Ba}_{1-x}\text{Ca}_x\text{Ti}_{1-y}\text{Zr}_y\text{O}_3$ (BCZT) films doping yttrium, which deposited on LaNiO_3 (LNO)/Au/Ti/SiO₂/HR-Si substrate by RF magnetron sputtering system, were obtained characteristic of low loss and high dielectric constant using DOE method at microwave frequency region.

Experimental

We analyzed first all of experimental factors, which may affect the high dielectric and low loss films, including substrate materials, buffer layer materials, electrode materials, sputtering parameters, target compositions, and measurement. A fishbone diagram for DOE procedures was made for screening the final experimental factors, depended on capabilities of control and technique in experiment. The diagram is showed in Fig. 1. Based on the DOE method, the substrate was determined the high resistivity (100) silicon wafer (HR-Si), as nearly neutral. The resistivity was greater than $15000\ \Omega\text{cm}$ and owned lower loss above 1GHz. The thickness of SiO₂ film was grown 200nm on Si wafer by RF magnetron sputtering to decrease leakage current from Si substrate. The bottom gold electrode was deposited 300nm on Ti film, 20nm thickness of buffer layer to enhance the adhesive strength between Au and SiO₂, by e-gun. The 90nm buffer layer of LaNiO_3 film, which plane has (001) prefer-orientation and perovskite structure to improve the performance of BZT or BST films, sputtered at 380°C in the $\text{Ar}/\text{O}_2=2:1$ atmosphere. All of the above factors were constant conduction.

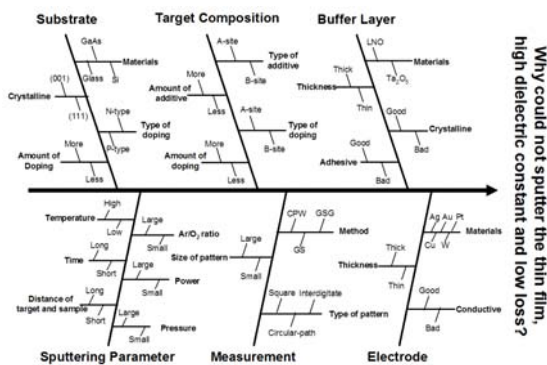


Figure 1. A fishbone diagram for DOE method

Table 1 is shown the comparison with factors and levels for DOE method. The factors were focused on changing BCTZ composition and substrate temperature of sputtering process. The $\text{Ba}_{1-x}\text{Ca}_x\text{Ti}_{1-y}\text{Zr}_y\text{O}_3$ film was also deposited with 5

mtorr pressure at 500~600°C in the $\text{Ar}/\text{O}_2=3:1$ by RF magnetron sputtering and used different composition targets, changed the mole fraction range including $x = 0-0.1$, $y = 0.15-0.25$, and doped 0-3 at% yttrium. The thickness of ferroelectric film was ~ 550nm. The interaction of the factors also is shown in table 1, due to Ca, Zr and Y ions may occupy A-site and B-site depended on A/B ratio and the changing grade of Curie temperature cause by amount of ions.

Table 1. Comparison of factors and levels for DOE method

Factor	Code	Level 1	Level 2	Interaction
substrate temperature	A	500°C	600°C	None
amount of Zr ions	B	y=0.15	y=0.25	
amount of Ca ions	C	x=0	X=0.1	
amount of Y doping	D	0	3 at%	

The factors were fitted in the suitable line-point diagram, and then created a $L_8 2^7$ orthogonal array for designed eight experiments in the first stage, which are shown in Fig. 2. The optimum conduction was based on the result of first stage to modify the experimental condition in the second stage. A top electrode of platinum and silver was sputtered on the BCTZ/LNO/Au/Ti/HR-Si film to form a MIM structure for below 1MHz and above 1GHz. The dimension of circular-path capacitor patterns, the inside radiuses throughout 30μm to 100μm and outside radius was hold on 125μm, was make by photolithography and chemical etching.

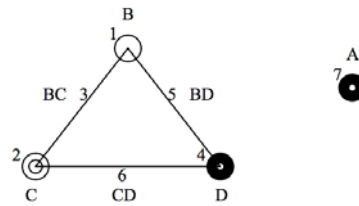


Figure 2. One of the line-point diagrams for $L_8 2^7$ orthogonal array

Figure 3 is appeared the diagram for MIM structure of ferroelectric film fabricated. The crystalline structure of LNO and BCTZ films were identified by x-ray diffraction (XRD, Rigaku, Dmax/IIB). The $\text{CuK}_{\alpha 1}$ line at $1.5405\text{\AA}$ was used as the diffraction source. The working voltage and working current were operated on 30KeV and 20mA, respectively. The range of screen angle, 2θ , was between 20-50 degrees. The microstructure and thickness of the all films were determined using a scanning electronic microscopy (FEGSEM, S6500). The device characteristics of the MIM capacitors were measured the dielectric properties at microwave

frequencies from 1-5 GHz to analyze with Agilent E8364A network analyzer.

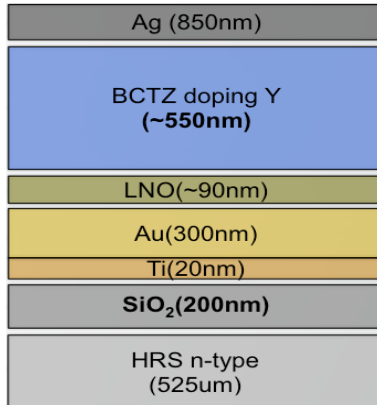


Figure 3. The diagram for MIM structure of ferroelectric film fabricated

Results and Discussion

The results of DOE method were based on eight targets of different composition, including No. 1 $\text{Ba}(\text{Ti}_{0.85}\text{Zr}_{0.15})\text{O}_3$, No. 2 $\text{Ba}(\text{Ti}_{0.85}\text{Zr}_{0.15})\text{O}_3 + 3 \text{ at\% Y}$, No. 3 $(\text{Ba}_{0.9}\text{Ca}_{0.1})(\text{Ti}_{0.85}\text{Zr}_{0.15})\text{O}_3$, No. 4 $(\text{Ba}_{0.9}\text{Ca}_{0.1})(\text{Ti}_{0.85}\text{Zr}_{0.15})\text{O}_3 + 3 \text{ at\% Y}$, No. 5 $\text{Ba}(\text{Ti}_{0.75}\text{Zr}_{0.25})\text{O}_3$, No. 6 $\text{Ba}(\text{Ti}_{0.75}\text{Zr}_{0.25})\text{O}_3 + 3 \text{ at\% Y}$, No. 7 $(\text{Ba}_{0.9}\text{Ca}_{0.1})(\text{Ti}_{0.75}\text{Zr}_{0.25})\text{O}_3$, and No. 8 $(\text{Ba}_{0.9}\text{Ca}_{0.1})(\text{Ti}_{0.75}\text{Zr}_{0.25})\text{O}_3 + 3 \text{ at\% Y}$. **Figure 4** is shown x-ray diffraction spectrum of eight compositions with different substrate temperature to deposited in the first stage of DOE. The (001) peak, which was a prefer-orientation, of LNO buffer layer had appeared in the all of samples. The crystalline of BCTZ films was compared with intensity and 2θ of (002) peak to determine the crystal structure, which are shown in **Fig. 5** and **Fig. 6**. Increased Ca ions caused to decrease the crystalline of films, according to No. 3, 4 was compared to No. 1, 2 and No. 7, 8 was compared to No. 5, 6. Also, increased Zr ions had the same results that were compared No. 5, 6 and No. 7, 8 to No. 1, 2 and No. 7, 8. The reasons were Ca ions replaced the sites of Ba, and Zr ions replaced the sites of Ti. The perovskite structure of BaTiO_3 was deformed to reduce the crystalline as the additive was enhanced.

The equation (1) is to calculate the lattice constant for c-axis of the crystal:

$$c = \frac{1.54056 \times (h^2 + k^2 + l^2)}{2 \sin\left(\frac{\theta}{2}\right)} \quad (1)$$

where c is lattice constant of c-axis, θ is the Bragg angle, h , k , and l are the index of plane direction. According the peak of (002) plane, the lattice constant was calculated between $4.07\text{--}4.13\text{\AA}$ as shows in **Fig.7**.

The lattice constant of BaTiO_3 in room temperature, $a=3.994\text{\AA}$ and $c=4.027\text{\AA}$, is small than the sputtered films at high temperature. The 2θ was shifted to high angle depended on the substrate temperature during sputtering process. The lattice constant of No. 2, 3, 5, and 8 was larger than the No. 1, 4, 6, and 7, respectively. **Figure 8** is shown the eight cross-sectional SEM images of ferroelectric films. The result of thickness was measured between $500\text{--}600\text{nm}$ from the SEM image.

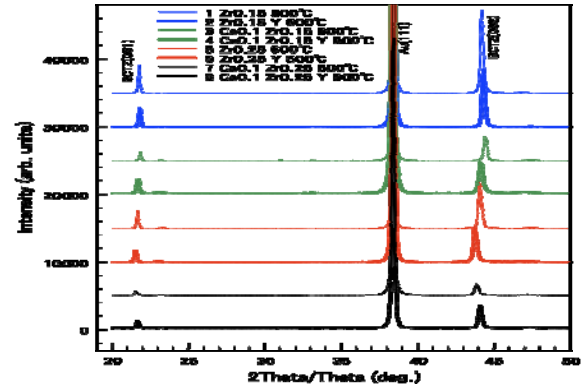


Figure 4. X-ray diffraction spectrum for eight compositions with different substrate temperature

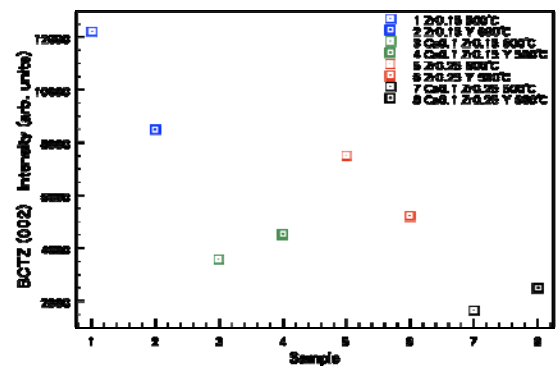


Figure 5. X-ray intensity of (002) peak for the crystalline BCTZ films

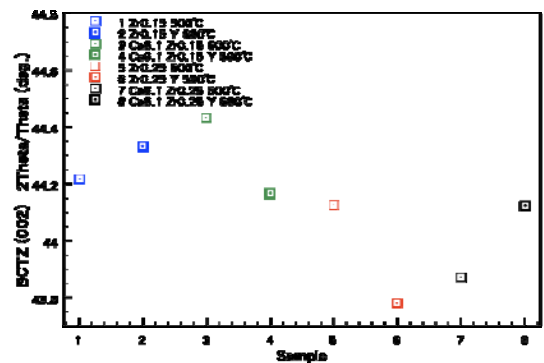


Figure 6. X-ray intensity of (002) peak for the change of Bragg angle

Using statistical ANOVA analysis, for the contribution percentage of the factors, the amount of Ca ions and substrate temperature were major influence factors on BCTZ films at microwave frequency. The results of ANOVA analysis for the electrical characteristic are listed in **Table 2**. The amount of Zr ions and the interaction between all of factors were influenced slightly and we neglect its effect to discuss the results. The substrate temperature was contributed 44% and 39% to affect the dielectric constant and loss tangent that caused of the structure were densification and less defect to obtain high dielectric constant and low loss. The quantity of Ca ions was provided for 14% and 39% contribution for electrical proprieties. The present investigation that adding Ca ions into ferroelectric film were decreased the maximum value of dielectric constant and diffusion phase transformation. [8] **Figure 9** is appeared the same result at microwave frequency that dielectric constant of No. 5 and No. 2 were also better than No. 3 and No. 8, individually. The range of dielectric constant was 73–91. **Figure 10** is shown the change of loss tangent depended on frequency at 1-5GHz. The loss tangent of No. 3, 4, 7, and 8 was lower than No. 2, 1, 6, and 5 due to add Ca ions in the films. The value of loss tangent was 0.055–0.105.

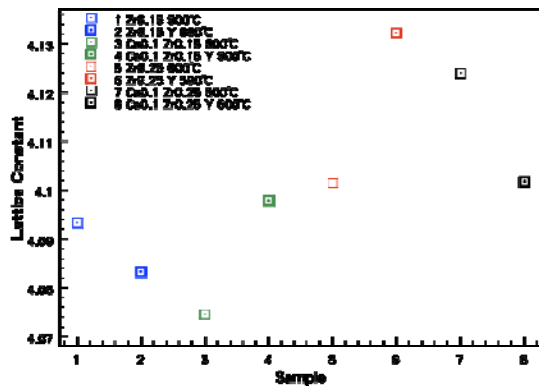


Figure 7. Lattice constant of c-axis for (002) plane of BCTZ films

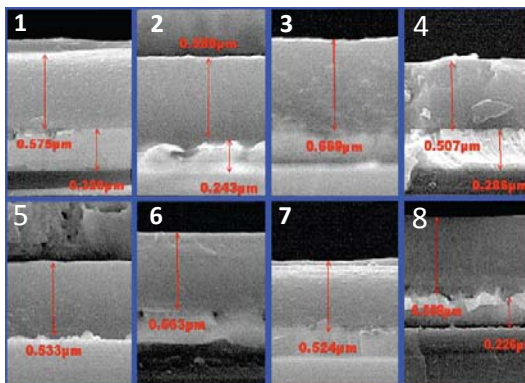


Figure 8 Cross-sectional SEM images of eight BCTZ films

Table 2. Summary of the characteristic results for the ANOVA analysis of BCTZ films

Loss tangent (the smaller the better)							
factor	A2 (Temp.)	B1 (Zr)	C2 (Ca)	D1(Y)	B1C2	C2D1	B1D1
notable	*		*				
contribution	39%	4%	39%	7%	10%	0%	1%
Dielectric constant (the bigger the better)							
factor	A2 (Temp.)	B1 (Zr)	C2 (Ca)	D1(Y)	B1C2	C2D1	B1D1
notable	*		*	*	*		*
contribution	44%	0%	14%	18%	8%	0%	16%
K value (the bigger the better)							
factor	A2 (Temp.)	B1 (Zr)	C2 (Ca)	D1(Y)	B1C2	C2D1	B1D1
notable	*		*	*	*		*
contribution	67%	3%	26%	1%	1%	3%	1%
Optimum constitute (Contribution percentage is a top priority.)							
condition	A2	B2 or B1	C2	D2			

The symbol “*” means the significance for the level of the factor.

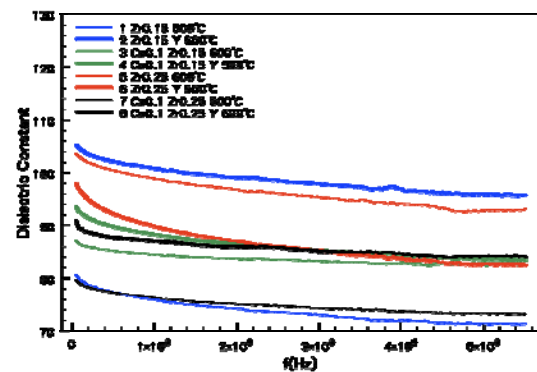


Figure 9. Variations of dielectric constant for BCTZ films at 1-5GHz

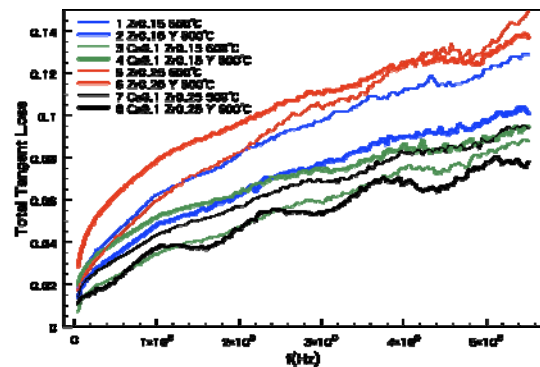


Figure 10. Variations of loss tangent for BCTZ films at 1-5GHz

Based on the objective of our research for high dielectric constant and low loss at microwave frequency, we defined a K value to evaluate the electrical performance by ANOVA analysis. The equation (2) of K value is:

$$K = \frac{\varepsilon}{\tan \delta} = \varepsilon \times Q \quad (2)$$

where ϵ is dielectric constant, $\tan\delta$ is loss tangent, and Q is quality factor. The K value was large that was exhibited a fine performance for the device. After calculating ANOVA analysis, the main factors also was the substrate temperature and amount of Ca ions, contributed 67% and 26%, respectively. The degree of accumulated contribution was significantly higher to approach 93%, represented to neglect almost the other factors to affect the proprieties.

We summarized the contribution percentage of the factors on multi-characteristic to provide the evidence of optimum condition for the second stage by DOE. In the **Table 2**, the factor of substrate temperature was inclined 600°C or higher (level 2) for dense crystalline structure. Amount of Ca ions was trend toward $x = 0.1$ (level 2) or more. The yttrium was enhanced the dielectric constant, the reason may occupy the defect site or shift the Curie point to room temperature nearly, but effected slight to loss tangent, favored the 3 at% Y doping (level 2). Amount of Zr ions at $y = 0.15$ -0.25 (level 1 and level 2) was varied lightly the electrical properties, as selecting mole fraction among 0.15 to 0.25. Therefore, the optimum condition of experimental in further work constitutes A2B2C2D2 or A2B1C2D2.

Conclusions

The $\text{Ba}_{1-x}\text{Ca}_x\text{Ti}_{1-y}\text{Zr}_y\text{O}_3$ films doping Y was fabricated on the $\text{LaNiO}_3/\text{Au}/\text{HR-Si}$ substrate by RF magnetron sputtering system. Using DOE Method to determine the optimization condition as adding 10 mol% Ca, 25 mol% or 15 mol% Zr, and Y doping 3 at% deposited temperature at 600°C or higher, the excellence dielectric properties which dielectric constant is 91 and lowest dielectric loss is 0.055 were appeared at 2.45GHz. Therefore, we will follow the optimized results to experiment in second stage by DOE method in the future.

References

- [1] G. W. Dietz, M. Schumacher, R. Waser, S. K. Streiffer, C. Basceri, and A. I. Kingon, "Leakage currents in $\text{Ba}_{0.7}\text{Sr}_{0.3}\text{TiO}_3$ thin films for ultrahigh-density dynamic random access memories", *J. Appl. Phys.* 82, pp. 2359-2364, 1997.
- [2] M. S. Tsai, S. C. Sun, and T. Y. Tseng, "Study of Multiferroic Properties in $\text{NiFe}/\text{BST}/\text{NiFe}/\text{BTO}$ Bilayer Thin Film System", *J. Appl. Phys.* 82, pp. 3482-3486, 1997.
- [3] W. Kwestroo and H.A.M. Paping, "The systems BaO-SrO-TiO_2 , BaO-CaO-TiO_2 , and SrO-CaO-TiO_2 ", *J. Am. Ceram. Soc.*, 42, pp. 292, 1959.
- [4] W. C. Yi, T. S. Kalkur, E. Philofsky, L. Kammerdiner, and A. A. Rywak, Appl., "Dielectric Properties of Mg-doped $\text{Ba}_{0.96}\text{Ca}_{0.04}\text{Ti}_{0.84}\text{Zr}_{0.16}\text{O}_3$ Thin Films Fabricated by Metalorganic Decomposition Method", *Appl. Phys. Lett.*, 78, pp. 3517, 2001.
- [5] R. V. Wang, P. C. McIntyre, J. D. Baniecki, k. Normura, T. Shioga, K. Kurihara, and M. Ishii, "Effect of Y Doping and Composition-Dependent Elastic Strain on the Electrical Properties of $(\text{Ba,Sr})\text{TiO}_3$ Thin Films Deposited at 520°C", *Appl. Phys. Lett.*, 87(19), pp. 192906, 2005.
- [6] W. J. Chou, C. H. Sun, G. P. Yu, and J. H. Huang, "Optimization of the deposition process of ZrN and TiN thin films on Si(100) using design of experiment method", *Material Chemistry and Physics*, 82, pp. 228, 2003.
- [7] H. J. Shy and T.B. Wu, "Structure and Electrical Characteristics of BaZrTiO_3 Thin Films Deposited on LaNiO_3 Electrode by RF Magnetron Sputtering", *Jpn. J. Appl. Phys.*, 37, pp. 5638, 1998.
- [8] S. Sen and R. N. P. Choudhary, "Effect of Doping Ca Ions on Structural and Electrical Properties of $\text{Ba}(\text{Zr}_{0.05}\text{Ti}_{0.95})\text{O}_3$ Electroceramics", *J. Mater. Sci.: Mater. in Electronics*, 15, pp. 671-675, 2004.