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A SYNTHESIS OF $BA_XSR_{1-X}TIO_3$ FILM AND CHARACTERIZATION OF FERROELECTRIC PROPERTIES AND ITS EXTENSION AS RANDOM ACCESS MEMORY

A. Hamdani[1*], M. Komaro[1], Irzaman[2]

[1]Department of Mechanical Engineering Education, Universitas Pendidikan Indonesia, Dr. Setiabudhi Street No. 207, Bandung, Indonesia.

[2]Department of Physics, IPB, Darmaga Street, Bogor, Indonesia.

*e-mail: aam_hamdani@upi.edu

Abstract. Ferroelectric material is generally used in engineering fields for such purposes as sensors, microelectronics, etc. It also provides more advantages compared to ferromagnetic materials, especially those related to a memory storage. This is due to a stored memory produced from magnetic system only consists of 105 bits/cm2 whereas a memory from ferroelectric can be stored up to 108 bits/cm^2. The objectives of this study were 1) to develop BST films on Pt (200) / SiO_2 / Si (100) substrates and p-type Si (100) substrates using the chemical solution deposition (CSD) method and 2) to test and study ferroelectric properties, XRD and SEM / EDS structure of the film produced. The research method used was an experiment, starting with the making of BST thin films, then ferroelectric tests, SEM / EDAX tests and XRD tests. The results of ferroelectric test show that all samples have ferroelectric properties. Therefore, annealing temperature affected a remanent polarization value and the coercive area of the sample. Regarding a memory application, BST ($BA_xSR_{1-X}TIO_3$)1 M sample with 900°C of annealing temperature is the best material to be used since they have a high remanent polarization and a low coercive field.

Keywords: annealing, BST, ferroelectric, ferromagnetic

1. Introduction

Random Access Memory (RAM) functions as a temporary data storage that can be run randomly when the computer is activated. The material of data storage in RAM is primarily made from ferroelectric thin films. It changes an internal polarization by using a proper electric field and spontaneous polarization of the material which determines a quality of the materials. Some main ferroelectric thin film materials consist of $BaSrTiO_3$, $PbTiO_3$, Pb ($ZrxTi_{1-X}$) O_3, $SrBaTaO_3$, Pb ($Mg_{1/3}Nb_{2/3}$) O_3 and $Ba_4Ti_3O_{12}$.

Among those ferroelectric thin film materials mentioned above, $BaxSr_{1-x}TiO_3$ (BST) is widely used as RAM since it has a high dielectric constant and high charge storage capacity [1]. A ferroelectric RAM which has a polarization value of about 10 μC.cm^{-2} may produce a charge of 1014 electrons per cm^{-2} for a memory reading process [2].

This study focused on the thin BST film on Pt (200) / SiO_2 / Si (100) substrates and p-type Si (100) substrates making through *Chemical Solution Deposition* (CSD) method which was then tested for ferroelectric, XRD, and SEM/EDS properties. In addition, BST was chosen because its manufacture can be simply done in a laboratory and in making it environmentally-friendly.

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2. Methodology

2.1 Materials

The materials used in this study were barium acetate powder [Ba $(CH_3COO)_2$, 99%], strontium acetate powder [Sr $(CH_3COO)_2$, 99%], titanium isopropoxide [$Ti(C_{12}O_4H_{28})$, 99.999%], solvent 2- methoxyethanol [H3COCH2CH2OH, 99%], Pt (200) / SiO2 / Si (100) substrate and p-type Si (100) substrate.

2.2 BST film making

Creating BST solvent. BST Solvent was made by utilizing barium acetate [Ba $(CH_3COO)_2$, 99%] + titanium isopropoxide [$Ti(C_{12}O_4H_{28})$, 99,999%] as *precursor* and 2-methoxyethanol [$H_3COOCH_2CH_2OH$, 99,9%] as solvents [3]. After all materials were mixed, the solvent was shaken for one hour. The produced solvent was then combined with acetic acid and then re-shuffled for 30 minutes. After that, it was heated to make all materials to be well-mixed. Finally, the solvent was filtered so that a more homogeneous solvent was obtained.

Preparing the substrates. This study used Pt (200) / SiO_2 / Si (100) and p-type Si (100) substrates. In producing the film, cleanliness of the substrate surface was an absolute requirement in order to produce it well and effectively.

Pt (200) / SiO_2 / Si (100) and p-type Si (100) substrates were washed by immersing them in methyl alcohol and then vibrating with ultra-sonic for about 5 minutes (until they were clean). After this process, it was dried by using nitrogen gas for 1 minute [4].

Growing the film. A substrate was put on a spin coating reactor which has been affixed with insulation in the middle position, then it was dripped with one drop of precursor solvent and rotated by using a spin coating reactor with a rotating speed of 3000 rpm for 30 seconds. This process was done 5 times to obtain 5 layers on the substrate. After that, the substrate was taken by using tweezers and dried by placing it on the surface of the iron which has been heated for 1 hour at approximate temperature of 120°C.

Annealing process. Annealing process was done by applying furnace Neberthem model Type 27. The substrates used were Pt (200)/SiO_2/Si (100) and Si (100) type-p substrate. Annealing was proceeded at the temperatures of 900°C, 950°C and 1000°C.

The annealing process was carried out gradually. The temperature of the furnace was regulated by increasing the temperature of 100°C per hour to the specified annealing temperature. Temperature detention was executed for 15 hours. Next, the cooling furnace was put into a room temperature. Regarding this, in general, the annealing process is presented in Fig. 1.

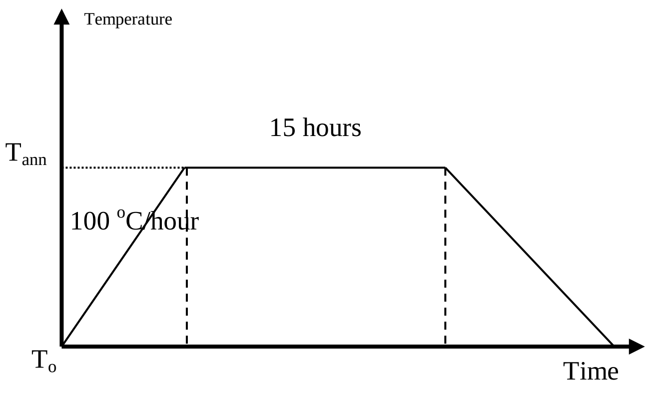


Fig. 1. Annealing process

2.3 Characterization

X-Ray diffraction. The XRD function is to determine the crystal system (cube, tetragonal, orthorhombic, rhombohedra, hexagonal, monocline, triclinic), resolve the quality of crystals (single crystal, poly crystal, amorphous), crystal symmetry, crystal defects, to reach crystal parameters (lattice parameters, distance between atoms, number of atoms per unit cell), identification of mixtures (e.g. in alloys) and chemical analysis. All observations are made from an angle of (2θ) 40° to 60° with an angle increasing to 0.02° every five seconds.

Ferroelectric test. This ferroelectric test aims to regulate the ferroelectric properties of the film obtained. The results of this test revealed saturation polarization values (Ps), remanent polarization (Pr) and coercive field (Ec) from the film. A thin film was also transformed into a structure as shown in Fig 2. Besides, this study employed a Radiant Technological A Charge Ver. 2.2. tool.

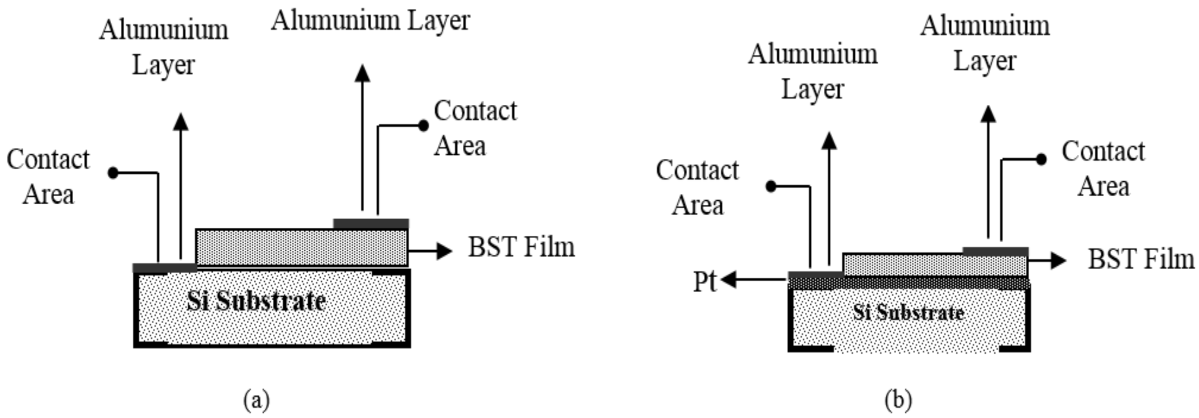


Fig. 2. Structure of Ferroelectric Test. (a) Ferroelectric test on Substrate Pt (200) /SiO_2/ Si (100), (b) Ferroelectric on Substrate Si (100) type-p

3. Results and discussion

The sample produced in this study can be seen in Table 1.

Table 1. Samples of the study

Sample Name	Substrate (s)	Annealing Temperature (^oC)
BST	Pt(200)/SiO_2/Si(100)	900
		950
		1000
	Si (100) type-p	900
		950
		1000

3.1. XRD test results

In this study, the XRD test was conducted with a diffraction angle of (2θ) 20° up to 80° with an increment angle of 0.02°. The XRD test results are displayed in Fig. 3.

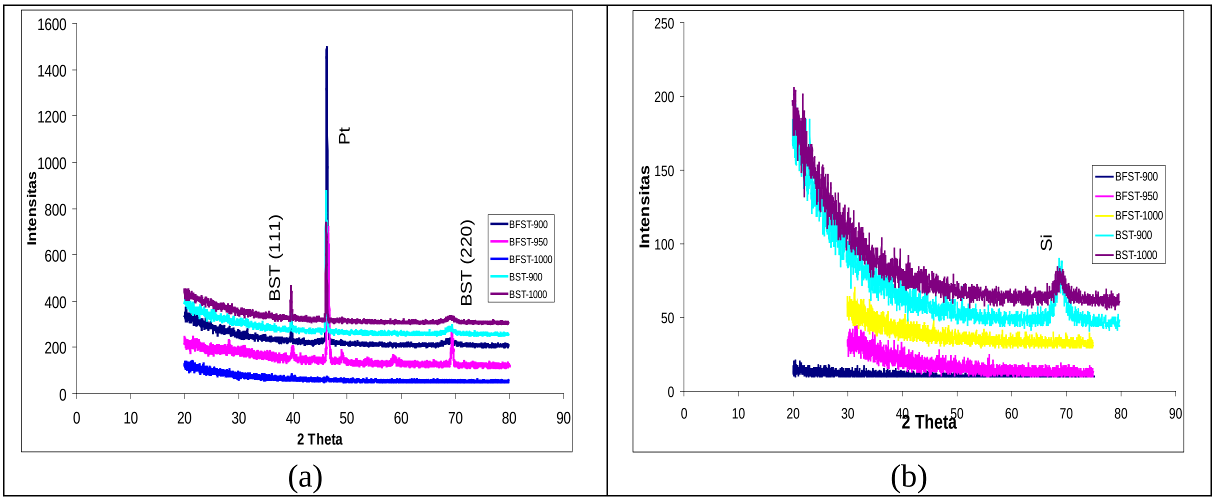


Fig. 3. XRD BST graphs for: (a) Pt (200)/SiO_2/Si (100) Substrate and (b) Si (100) Type-p Substrate

In Figure 3, it demonstrates the increment of annealing temperature casuing differences in the nature of the film. All samples grown on the Si (100) substrate have been damaged. In contrast, not all samples grown on substrate Pt (200) / SiO_2 / Si (100) were broken. According to Adem (2003), platinum (Pt) is very well used as a bottom electrode for thin-film ferroelectric-dielectric devices because it has a high thermal conductivity (71.6 $Wm^{-1}K^{-1}$) and good stability in an oxygen atmosphere [5].

The higher the temperature of annealing is, to a certain extent, the better the quality of the ctrystal gets. However, too high annealing temperature may impair the crystal. It is indicated in BST samples raised on Pt (200) / SiO_2 / Si (100) substrates, the samples were broken at higher annealing temperatures.

Increasing chemical substances may also affect the sample. BST film layer is crystalizing when the annealing temperature is 1000°C mixed with Pt (200) / SiO_2 / Si (100) substrate, while the same treatment to BFST thin film may also be distracted.

Based on the calculation of lattice constants, it is stated that all samples are tetragonal, as presented in Table 2.

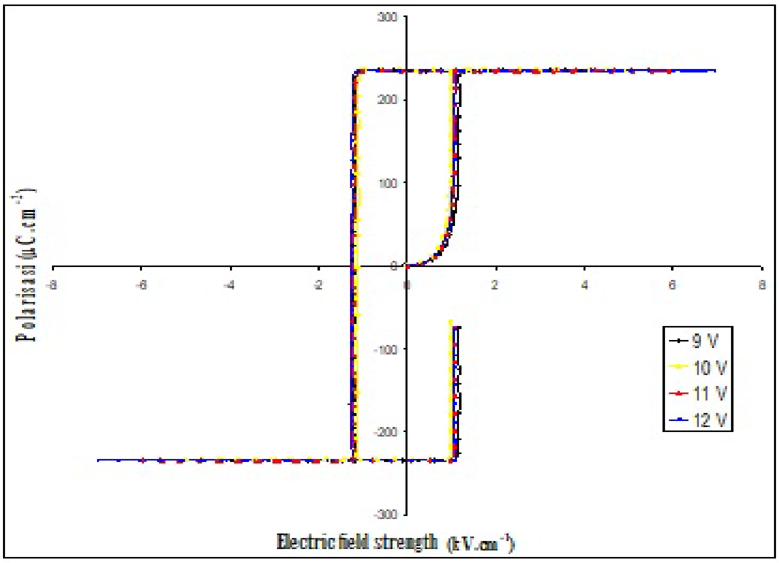
Table 2. The calculation result of BST parameter lattice sample

Types of Sample	Lattice Parameter (Å)			Crystal Shape
	A	C	c/a	
BST-Pt-900	3,8469	4,1174	1,0703	tetragonal
BST-Pt-1000	3,8472	4,1137	1,0693	tetragonal
BST-Si-900	-	-	-	damaged
BST-Si-1000	-	-	-	damaged

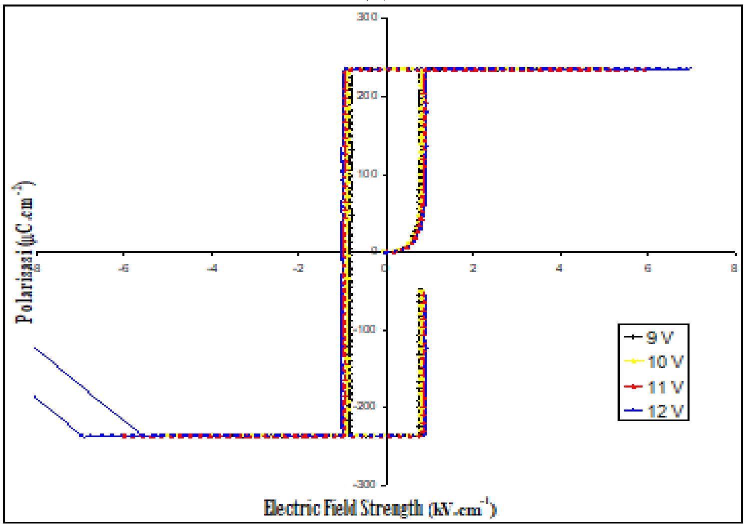
3.2. Ferroelectric test results

The results demonstrate that all samples made, both BST 1 M and BFST 1 M 10%, were ferroelectric. It can be seen from the hysteresis curve formed from each sample. The treatment of differences in annealing temperature, increasing of chemical substances and subtracting differences also influenced the parameter values obtained from ferroelectric tests. In this study, ferroelectric tests were carried out by providing voltage variations from 5 V to 13 V.

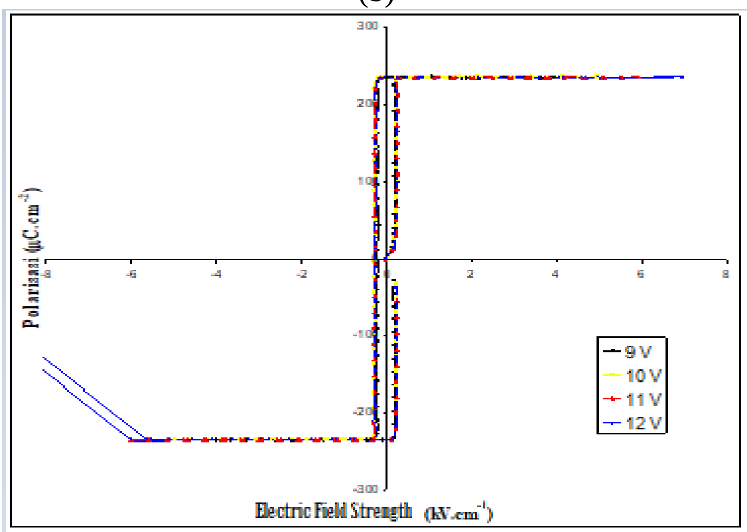
The hysteresis curve of BST 1 M film on Pt (200) / SiO_2 / Si (100) substrates can be seen in Fig. 4.



(a)



(b)



(c)

Fig. 4. Hysteresis curve of BST 1 M on Pt (200)/SiO_2/Si (100) Substrate with annealing temperature 900°C (b) 950°C (c) 1000°C

Figure 4 shows that the greater the voltage applied, the curvier the shape will be. On the curve (a), the width of the curve displays the field strength (kV.cm-2) measured in the sample. This is because the voltage increment causes more orientation of parallel domains so that the strength of the terrain will increase [5].

In BST 1 M film samples with 950 and 1000°C annealing temperatures (see curves b and c in Fig. 4), the curves were no longer perfect. This indicates that the voltage given to the sample has passed the breakdown voltage which causes the sample to no longer be in a ferroelectric state but it has become paraelectric a situation where the sample has no longer spontaneous polarization [5].

Moreover, in Fig. 5, it can be identified that the BST hysteresis curve is varied by an external stress and annealing temperature.

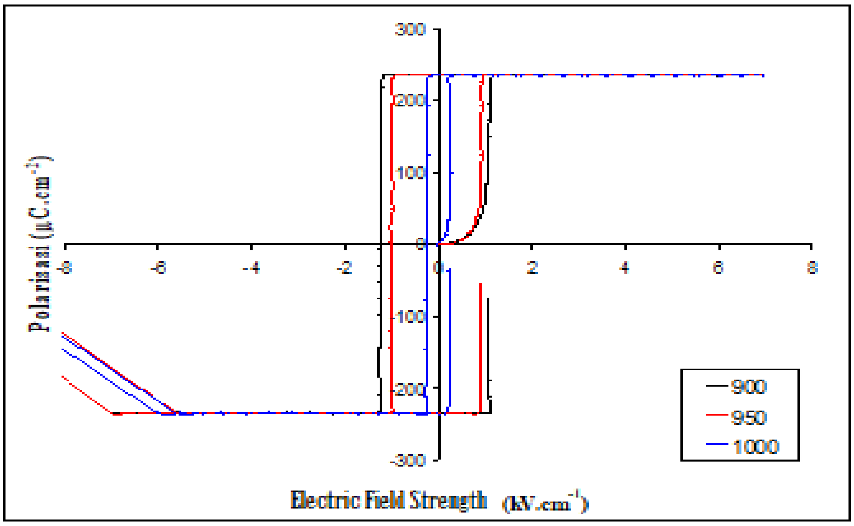


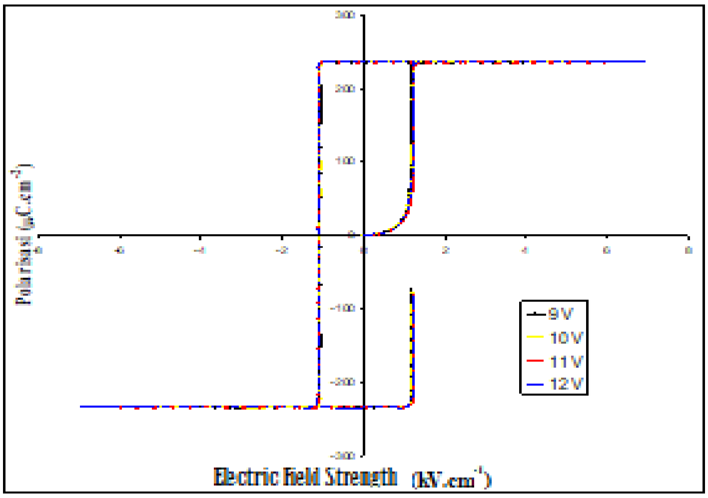
Fig. 5. Hysteresis curve BST 1 M on Pt (200)/SiO_2/Si (100) Substrate to the varied *Annealing* temperature

The variation of external voltage and temperature of annealing slightly affect sample saturation polarization. After saturation is achieved, the voltage does not increase to the saturation polarization value because in this situation, all domains have been oriented in the same direction [5]. After the saturation state, the greater external voltage will cause the sample to lose its ferroelectric properties. Besides polarization, the annealing temperature also affected the remanent polarization (Pr) and the coercive field strength (Ec).

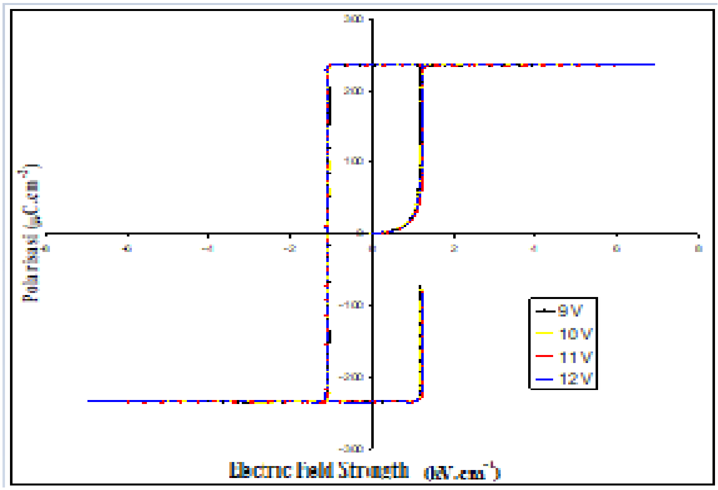
Regarding the remanent polarization (Pr) (see Fig. 5), the higher the annealing temperature, the lower the remanent polarization values can be obtained. The remanent polarization value is lower due to the smaller and standardized grain size [5].

For coercive field values (Ec), this result is in a good agreement with literature. According to Koutsaroff et al., the temperature of annealing leads to the grain size formed in the sample. As a result, the higher the temperature, the more grain size formed [6]. Under the size of the critical grain size, there is a transition from a multi-domain structure to a more stable mono-domain. Hence, re-orienting the domain in an external electric field becomes more difficult as it is increasing the coercive field [7]. In BST samples grown on Pt (200) / SiO_2 / Si (100) substrates, the increment of annealing temperature influenced the grain size to be smaller (this can be seen from the XRD peak shape) and the sample coercive field decreased (see Fig. 5).

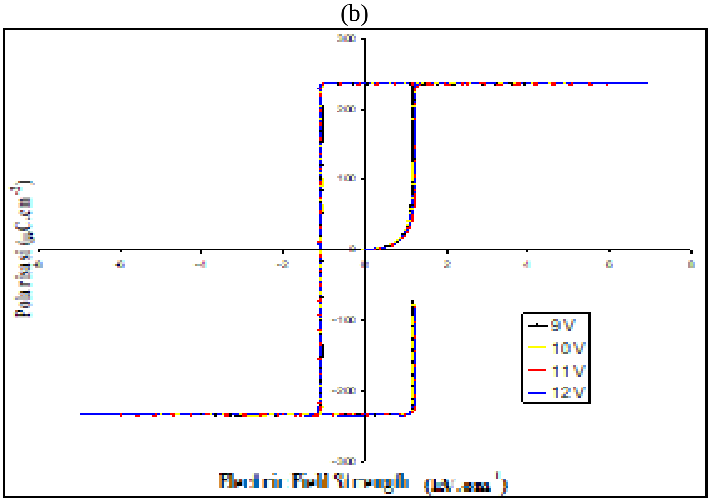
The BST 1 M film hysteresis curve on p-type substrate Si (100) can be seen in the Figs. 6a, 6b, and 6c.



(a)



(b)



(c)

Fig. 6. Hysteresis curve of BST 1 M on Si (100) type-p substrate to the annealing temperature (a) 900, (b) 950, and (c) 1000°C

Figure 6 (a) displays the results of ferroelectric test showing that the greater the voltage applied, the more curved the shape of the figure- or commonly known as *Ferroelectric*. For curves (b) and (c) at external voltages of 12V, the curves formed were no longer perfect. Consequently, the sample did not act as ferroelectric but it became a *paraelectric*.

Figure 7 presents hysteresis curve of BST which is varied by annealing temperature.

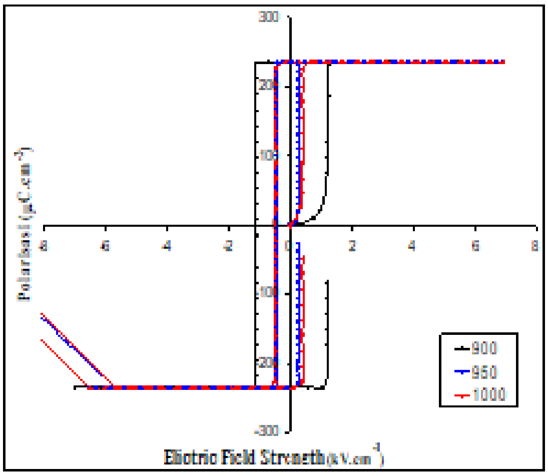


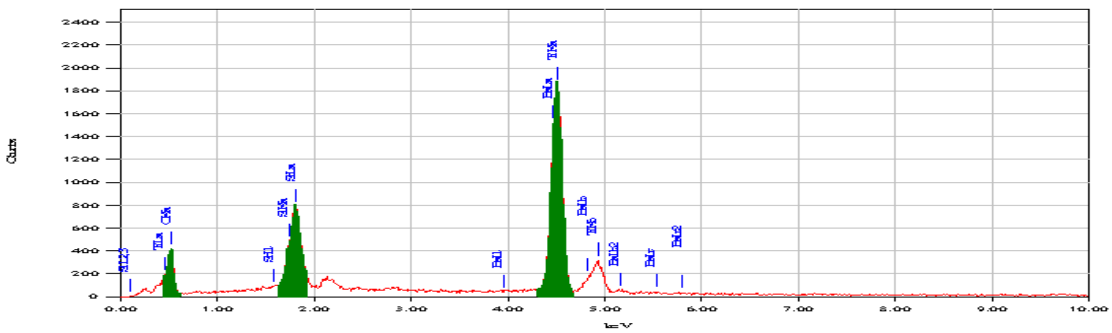
Fig. 7. Hysteresis curve BST 1 M on Si (100) Type-p Substrate to the varied annealing temperature

In addition, variation of external voltage and temperature of annealing slightly affected a sample of saturation polarization. Once it was done, the addition of external voltage did not change the saturation polarization value since all domains had been oriented in the same direction [5].

In BST 1 M samples increased to p-type Si (100) substrate, annealing temperature increment caused the remanent polarization values and decreased a coercive field. This is due to the condition of the sample that had been damaged.

3.3. An Analysis of SEM/EDS

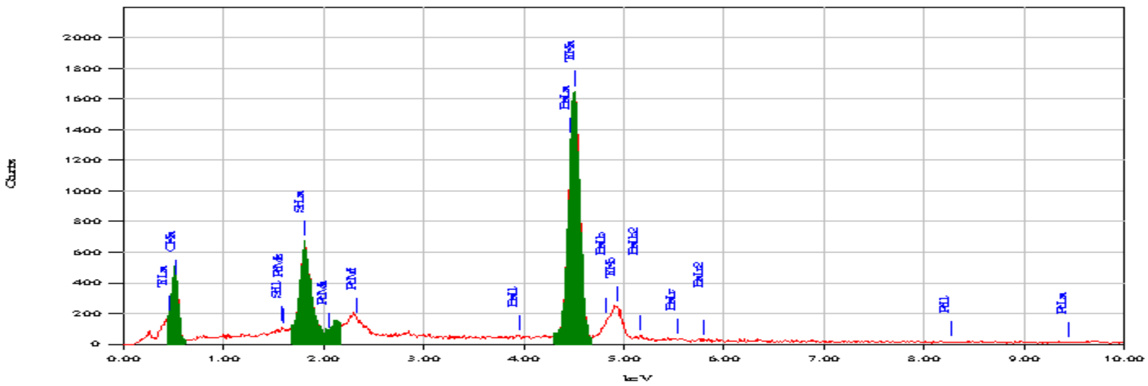
SEM / EDS analysis is required to determine the phases and chemical compositions. Observations from the results of SEM / EDS are presented in Fig. 8.



Element		(keV)	mass%	Error%	At%	Compound	mass%	Cation	K
O K		0.525	10.68	0.30	36.83			6.4652	
Si K	*	1.739	3.31	0.16	6.50			2.4041	
Ti K		4.508	24.92	0.24	28.70			28.1464	
Sr L		1.806	15.04	0.50	9.47			13.2026	
Ba L	*	4.464	46.04	0.58	18.49			49.7817	
Total			100.00		100.00				

Fig. 8. The results of EDS to BST (Anil 1000°C) on Pt Substrate

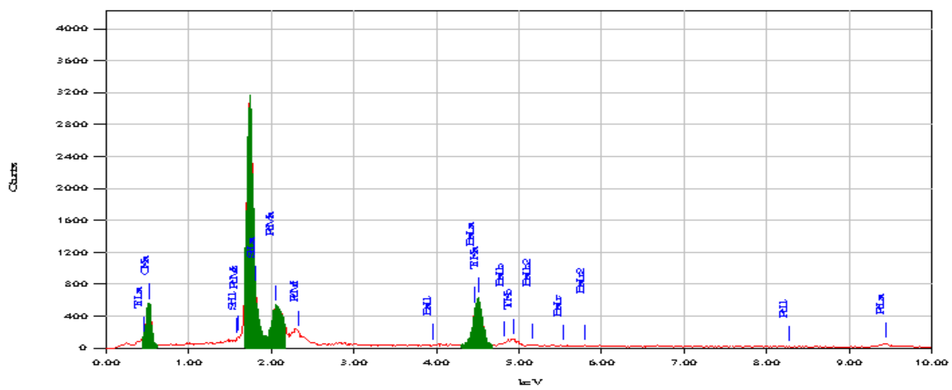
From the SEM / EDAX BST data shown previously, Si (100) at annealing temperature of 1000°C, Ba, Sr and Ti elements were detected.The results of SEM / EDAX BST on Pt (200) at annealing temperature of 900°C, are displayed in Fig. 9.



Element		(keV)	mass%	Error%	At%	Compound		mass%	Cation	K
O			22.02							
Ti K		4.508	22.06	0.41	50.57	TiO2	36.79	8.03	30.1653	
Sr L		1.806	10.92	0.50	13.69	SrO	12.92	2.17	11.4065	
Ba L	*	4.464	43.98	0.68	35.17	BaO	49.11	5.58	57.5894	
Pt M	*	2.048	1.01	0.66	0.57	PtO2	1.18	0.09	0.8388	
Total			100.00		100.00		100.00	15.88		

Fig. 9. The results of SEM/EDAX BST on Pt (200) of annealing temperature 900°C

Results of SEM / EDAX, BST data on Pt substrate (200) at annealing temperature of 900°C, Ba, Sr and Ti elements were detected. Whereas if the annealing temperature of 1000°C, Sr element is no longer detected as presented in Fig. 10.



Element		(keV)	mass%	Error%	At%	Compound	mass%	Cation	K
O K		0.525	26.28	2.38	70.29			21.2379	
Ti K		4.508	15.70	2.32	14.03			18.8654	
Sr L	*								
Ba L	*	4.464	32.11	5.70	10.00			36.9174	
Pt M	*	2.048	25.90	4.34	5.68			22.9793	
Total			100.00		100.00				

Fig. 10. The Results of SEM/EDAX BST on Pt (200) Substrate of annealing temperature 1000°C

4. Conclusion

BST film has ferroelectric properties as shown from the hysteresis curve produced based on ferroelectric tests. The temperature of annealing has a dominant influence on the value of the coercive field and a remanent polarization. This is due to the fact that the higher the annealing temperature, the greater the grain size produced. However, too high annealing temperature may also affect the sample to suffer a damage as resulted in a decrease in the coercive field value and the remanent polarization of the sample. After saturation has been achieved, the greater external voltage will lose ferroelectric properties of the sample. Film samples grown on Pt (200) / SiO_2 / Si (100) substrates, and increment of chemical material cause the coercive field value and breakdown voltage to increase. As for the p-type Si (100) substrate, the increment of chemical material is not clearly visible since the sample has been damaged. For memory applications, BST 1 M samples with annealing temperature of 900°C are the best option because they have a high remanent polarization and a low coercive field.

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