Fabrication of $Pb(Zr,Ti)O_3$ Thin Film for Non-Volatile Memory Device Application

Mar Lar Win

Metallurgical Research and Development Centre (Ela)
Ministry of Science and Technology , Myanmar

marlarwin99 @gmail.com

Abstract*—Ferroelectric lead zirconate titanate powder was composed of mainly the oxides of titanium, zirconium and lead. PZT powder was firstly prepared by thermal synthesis at different Zr/Ti ratios with various sintering temperatures. PZT thin film was fabricated on SiO_2/Si substrate by using thermal evaporation method. Physical and elemental analysis were carried out by using SEM, EDX and XRD The ferroelectric properties and the switching behaviour of the PZT thin films were investigated.The ferroelectric properties and switching properties of the PZT thin film (near morphotropic phase boundary sintered at 800ºC) could function as a nonvolatile memory.

***Keywords*— lead zirconate titanate, thermal evaporation, SEM EDX , XRD ,coercive field , remanent polarization,transient current**

I. INTRODUCTION

Ferroelectric materials have (a) high dielectric constant (b) high piezoelectricity (c) relatively low dielectric loss (d) high electrical resistivity and (e) high electro-optic coefficients which make them attractive for a variety of application. Ferroelectric thin films ($BaTiO_3$, $PbTiO_3$, $Pb(Zr,Ti)O_3$, $Pb(La,Zr)TiO_3$, $KNbO_3$, $LiNbO_3$ and $PbZrO_3$), have been investigated for a wide variety of electrical and optical applications.

The non - volatile operation of FeRAM is based on the hysteresis characteristics of ferroelectric perovskite materials, such as PZT($Pb(Zr,Ti)O_3$ and SBT ($Sr(Bi,Ta)O_3$). Two stable points at zero electric field, the remanent polarization (± Pr) are used for the non-volatile operation of "0" and "1" states. This is a nonvolatile storage element since the data is present when the voltage is removed. No applied field or voltage is required to maintain the memory, which is why the device is termed "nonvolatile".

Ferroelectric thin films are promise of the important applications such as nonvolatile memory, ferroelectric random access memories,electro - optic waveguide, thin film capacitor, optical modulator, detector, ferroelectric gates (FETs) and metal/insulator/semiconductor transistor device (MIST), metal/ ferroelectric/ semiconductor (MFS) capacitors, metal/ ferroelectric/ insulator/ semiconductor (MFIS) capacitors and ferroelectric memory diode (FMD).

A variety of deposition methods have been proposed for ferroelectric thin films. The methods receiving the most attention are chemical vapor deposition (CVD), sputtering, evaporation, metal organic chemical vapor deposition (MOCVD), molecular beam epitaxy (MBE), sol - gel and metal organic deposition (MOD). They can be divided into dry and wet process. The first five methods are dry processes and are usually required hot substrates. Some of them are relatively slow and expensive but allow greater ease of epitaxial film growth and are still widely used. The last two methods are wet processes and low deposition temperature. They are fast and inexpensive. The ferroelectric thin films are deposited on a variety of substrates including sapphire, silicon, GaAs, fused silica, Pt - coated Al_2O_3, single crystal MgO and $MgAl_2O_4$ and single crystals of several ferroelectrics.

In this paper, the PZT thin films were deposited by thermal evaporation process.Thermal evaporation technique had received considerable attention because of simple and inexpensive method to produce ferroelectric thin film.In this work ,thermal evaporated PZT thin films were fabricated on SiO_2/Si substrates. Physical and elemental analysis was carried out. Ferroelectric properties and switching behaviour of all PZT films were investigated.The aim of the present work is to select the most suitable characteristics of the PZT thin film with various Zr/Ti ratios for FeRAM device.

II. EXPERMENTAL PROCEDURE

The starting materials lead oxide (PbO), titanium oxide (TiO_2) and zirconium oxide (ZrO_2) are mixed in various Zr/Ti ratios and then calcined in the atmosphere. There are four chemical processes, i.e.,

(T< 350ºC) : no reaction;
(350ºC <T< 650ºC) : $PbO + TiO_2 \rightarrow PbTiO_3$;
(650ºC<T<800ºC) : $PbTiO_3 + PbO + ZrO_2 \rightarrow Pb(Zr_{1-x}Ti_x)O_3$;
(800ºC<T<1100ºC): $Pb(Zr_{1-x}Ti_x)O_3 + PbTiO_3 \rightarrow Pb(Zr_{1-x'}Ti_{x'})O_3$; (x < x')

Where T is calcined temperature.

Ferroelectric lead ziroconate titanate powder show Ti-rich compositions ($0 \leq x \leq 0.53$), a tetragonal region whereas compositions with lower Ti-content ($0.53 \leq x \leq 0.94$), a rhombohedral region. Both regions are separated by a morphotropic phase boundary at x = 0.53. It is clear that the combination reaction of lead zirconate titanate (PZT) powder is essentially completed about 800ºC. To obtain the calcined PZT powder, PbO, ZrO_2 and TiO_2 are mixed in various Zr/Ti ratios and calcined in crucibles at 800ºC for 2h. Prior to the coating, the p-Si (100) substrates (resistivity ρ 1 ~ 15 Ωcm) are cleaned using Standard Cleaning Procedures. Organic and metallic contaminations are removed by etching the solution

(HF: HO_2 = 1:5). Metallic contamination represents of the major causes of device performance loss. It includes mobile charge in oxides producing functional defects. The substrates are immersed in deionized water for 20 min. Then, the substrates are cleaned and washed in acetone and isopropyl alcohol and drying the substrates.

The deposition of perovskite type lead zirconate titanate thin film on bare Si is difficult because of the diffusion of Pb and Ti into the Si substrate. In order to obtain a good interface, SiO_2 layer has been introduced as a buffer layer between the PZT thin film and Si substrate. The formation of SiO_2, layer occurs during the subsequent annealing on p-Si (100) substrates. There are many fabrication methods among them thermal evaporation process is simple and inexpensive method to fabricate PZT thin film. The calcined PZT powders are evaporated onto the surface at various sintering temperatures for 2 h. The surface morphology has been investigated by SEM. The elemental compositions of the PZT thin film is analyzed by energy dispersive X-ray (EDX). The orientation is determined by X-ray diffraction (XRD). The ferroelectric properties and switching behavior of the PZT thin films are also examined.

III. RESULT AND DISCUSSION

A. SEM, EDX and XRD Analysis

The surface morphology of the PZT thin film is characterized by SEM. Figure 1 shows the SEM of PZT thin films at Ti-rich region, near morphotropic phase boundary and Zr-rich region respectively. All these films are adherent crack free form and did not observe fine gain size. In thermal evaporation process, the structures of PZT thin films are generally disordered because of its crystal growth mechanism. From SEM observation, the structures of PZT thin film (near morphotropic phase boundary) sintered at 800ºC promoted the agglomeration action of particles.

The elemental compositions of the PZT thin film is analyzed by EDX. Figure 2 shows analysis EDX analysis of the PZT thin film (near morphotropic phase boundary) sintered at 800ºC. It indicates that the PZT thin film consists of Pb, Zr, Ti and O element. From EDX analysis, Pb, Zr, Ti, Si and O peaks are combined with each other. These combined peaks indicated that the PZT thin films is good adhesion on the substrate by thermal evaporation process.

X-ray diffraction analyse is used to study phase formation and transformation, lattice parameters, the preferred orientation of the PZT thin film. The crystal structure of the PZT thin film is characterized by X-ray diffraction. Figure 3 pattern of the PZT thin film (near morphotropic phase boundary) sintered at 800ºC. In this case, it is shown that there exists (001), (100), (111), (200), (220) and (310) peaks from PZT film, which confirmed that the PZT film has a pervskite phase, and the sharpness of the five peaks indicates good crystallinity. The intensity of this X-ray pattern increases up to the highest temperature 800ºC. The structure of perovskite PZT is identified for the film made at 800ºC.From the XRD analysis, the PZT thin film (near morphotropic phase boundary) sintered at 800ºC has good tetragonality and perovskite structure.

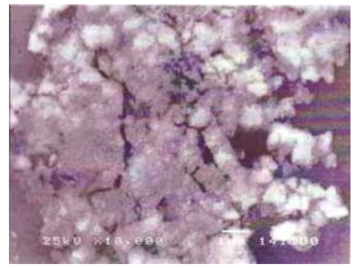

Fig 1(a). SEM micrograph of Pb (Zr, Ti)O_3 thin film at Ti – rich region

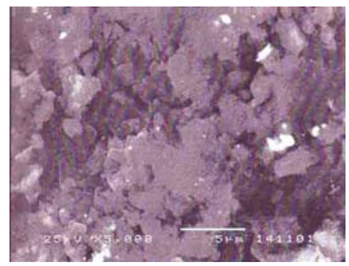

Fig 1(b). SEM micrograph of Pb (Zr,Ti)O_3 thin film near morphotrophic phase boundary

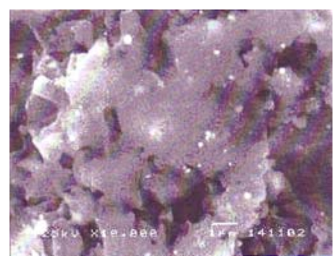

Fig 1(c). SEM micrograph of Pb (Zr,Ti)O_3 thin film at Zr-rich region

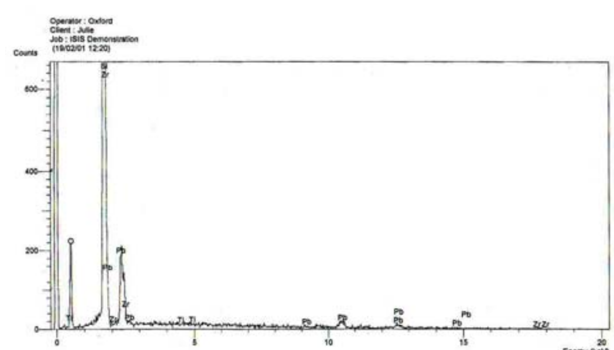

Fig 2. EDX pattern of Pb ($Zr_{0.54}$, $Ti_{0.46}$)O_3 thin film sintered at 800°C

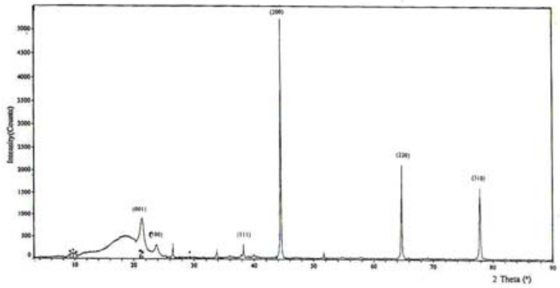

Fig 3.XRD pattern of Pb ($Zr_{0.54}$, $Ti_{0.46}$)O_3 thin film sintered at 800°C

B. Ferroelectric Properties and Switching properties Measurement

An important characteristics of ferroelectric is the ferroelectric hysteresis loop. The hysteresis loop is the intrinsic characteristic of ferroelectric, which is always measured with the Sawyer-Tower circuit to test the ferroelectricity of the films. The frequency used in the Sawyer – Tower circuit to measure the hysteresis loop and where the heating effects of high frequency signals cause distortion of the hysteresis loop.

Table 1(a) shows list of the value of P_r(remanent polarization) and E_c(coercive field) of the PZT thin film at various Zr/Ti ratios sintered at 800ºC. This table indicates that the sample D (near morphotropic phase boundary)has high remanent polarization and low coercive field.Ferroelectric properties of sample D is better than the Ti-rich and Zr-rich samples.

Table 1(b) expresses the ferroelectric properties of Pb($Zr_{0.54}Ti_{0.46}$)O_3 sintered at various sintering temperatures for 2h.This table shows Pb($Zr_{0.54}Ti_{0.46}$)O_3 thin film (near morphotropic phrase boundary) sintered at800ºC for 2h has better ferroelectric properties than other sintering temperatures.As show in figure 4 a, b and c by improving the crystallinity which increasing sintering temperature, an improvement in saturated characteristics of the P-E hysteresis loop was confirmed. From these result the Pb($Zr_{0.54}$ $Ti_{0.46}$)O_3 thin film sintered at 800ºC exhibit excellent behavior as indicated by large remanent polarization and low coercive field.

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Fig 4. (a) Ferroelectric hysteresis loop of Cu/PZT/SiO_2/Si structure sintered at 700°C (x : 21 kV/cm ; y ; 40 μC/cm^2)

Fig 4.(b) Ferroelectric hysteresis loop of Cu/PZT/SiO_2/Si structure sintered at 800°C (x : 21 kV/cm ; y ; 45 μC/cm^2)

Fig 4. (c) Ferroelectric hysteresis loop of Cu/PZT/SiO_2/Si structure sintered at 900°C (x : 22.5 kV/cm ; y ; 32μC/cm^2)

TABLE I(a)
List of ferroelectric properties at Ti-rich region near morphotropic boundary and Zr-rich region sintered at 800°C

Sample	**Pb(Zr_xTi_{1-x})O_3 x**	**Region**	**P_r (μC/cm^2)**	**E_c (kV/cm)**
A	20	Ti-rich	36	18
B	30	Ti-rich	39	19.5
C	40	Ti-rich	43	20
D	54	Near morphotropic phase boundary	45	21
E	60	Zr-rich	37	21
F	70	Zr-rich	34	23
G	80	Zr-rich	31	24

TABLE I(b)
List of ferroelectric properties of Pb(Zr_xTi_{1-x})O_3 thin film at various sintering temperatures

Sample	sintering temperature T_s(°C)	**P_r (μC/cm^2)**	**E_c (kV/cm)**
D	500	35	20
	600	38	20
	700	40	21
	800	45	21
	900	32	22.5
	1000	28	24

Another important characteristic of ferroelectric is the switching behavior of the PZT thin film can be observed by switching characterization circuit. The bipolar square pulses with a frequency of 60 kHz are applied to the circuit. When the spontaneous polarization reverses, a displacement current flows in the crystal causing an equal "real" current to flow in the resistors. The later current "I" can be displayed on an oscilloscope as a function of time "t". The current due to the reversal of the polarization is called the "switching current" or the "transient current". The transient currents for charging and discharging were determined by measuring the voltage drop through the resistor. The electric charge was calculated by integrating the transient currents. The switching characteristics of the PZT thin films are studied by using Cu electrode.

Table 2(a) indicates that the transient current(near morphotropic phase boundary) sintered at 800ºC is maximum.From this table,the transient current at Zr-rich region exhibited slow polarization reversal.At near morphotropic phase boundary, the transient current is maximum due to high polarization reversal.The sampleD sintered at 800ºC has good polarization reversal (switching behaviour)than the other samples such as Ti-rich and Zr-rich samples.According to table 2(b),it shows that the transient current of the sampled sintered at 800ºC for 2h has maximum value and is confirmed that the PZT thin film is good crystallization at high temperature 800ºC in the present method.

$Pb(Zr_{0.54}\ Ti_{0.46})O_3$ thin film of MFIS structure sintered at 700ºC, 800ºC and 900ºC. The maximum transient current of $Pb(Zr_{0.54}\ Ti_{0.46})O_3$ thin film sintered at 800ºC is I_{max} = 62.55 µA. From these result; the sample D (near morphotropic phase boundary) sintered at 800ºC has the good polarization reversal (switching characteristics) than the other samples.

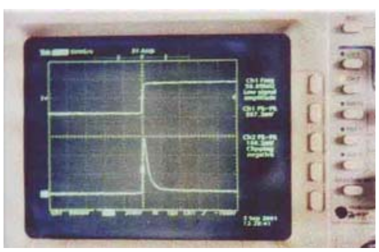

Fig 5. (a) Switching transient current of $Pb(Zr_{0.54}\ Ti_{0.46})O_3$ thin film Cu/PZT/SiO_2/Si structure sintered at 700°C (I_{max} =50.1µA)

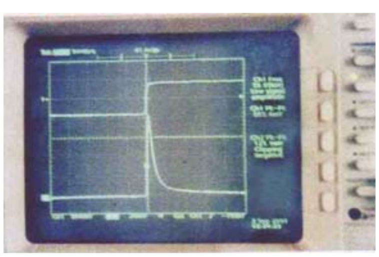

Fig 5. (b) Switching transient current of $Pb(Zr_{0.54}\ Ti_{0.46})O_3$ thin film Cu/PZT/SiO_2/Si structure sintered at 800°C(I_{max} =62.55µA)

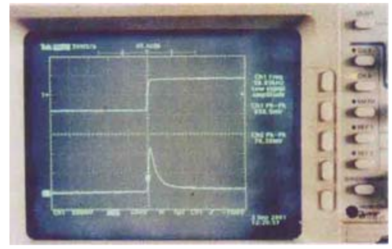

Fig 5. (c) Switching transient current of $Pb(Zr_{0.54}\ Ti_{0.46})O_3$ thin film Cu/PZT/SiO_2/Si structure sintered at 900°C(I_{max} =35.19µA)

TABLE III (a)
List of maximum transient current at Ti-rich region ,near morphotropic boundary and Zr-rich region sintered at 800°C

Sample	$Pb(Zr_xTi_{1-x})O_3$ x	Region	T_s(°C)	I_{max} (µ A)
A	20	Ti-rich	800	50.9
B	30	Ti-rich	800	54
C	40	Ti-rich	800	58.7
D	54	Near morphotropic phase boundary	800	62.55
E	60	Zr-rich	800	47.4
F	70	Zr-rich	800	44.6
G	80	Zr-rich	800	40.18

TABLE II(b)
List of maximum transient current of $Pb(Zr_xTi_{1-x})O_3$ thin film at various sintering temperatures

Sample	sintering temperature T_s(°C)	I_{max} (µ A)
D	500	36.22
	600	45.96
	700	50.1
	800	62.55
	900	35.19
	1000	29.7

IV. CONCLUSIONS

Lead zirconate titanate thin films are deposited onto p-Si (100) wafers by using thermal evaporation method. The surface morphology has been investigated by SEM. The elemental compositions of the PZT thin film is analysed by EDX. The orientation of PZT thin film is investigated by X-ray diffraction(XRD). The intrinsic behaviour of the ferroelectric hysteresis loops are observed by the Sawyer - Tower circuit. The PZT thin film (near morphotropic phase boundary) sintered at 800ºC showed the remanent polarization P_r = 45 µC/cm^2 and the coercive field E_c = 21kV/cm. The switching behavior is measured by the switching characterization circuit. The maximum transient current of the PZT thin film (near morphotropic phase boundary) sintered at 800ºC was I_{max} = 62.55 µA. According to the experimental result, it is believed that the PZT thin film (near morphotropic phase boundary) sintered at 800ºC can be used for the fabrication of FeRAM due to its high remanent polarization, low coercive field and maximum transient current.

ACKNOWLEDGEMENT

The author thanks my respectable professor Dr.Myint Kyi (Pro-Rector),Dr. Ko Ko Kyaw Soe, Dr. Tun Khin for his supervision and professor Dr.Khin Maung Latt for helpful discussions and technical assistance and also thanks my mother and sisters for their encouragements.

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