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Fabrication and Memory Behaviour of Al (6 mol%) Doped $PbTiO_3$ Thin Film Devices

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Abstract— The polycrystalline perovskite structure of $PbTi_{(1-x)}Al_{(x)}O_3$ (x=0.06), PTA6, was obtained by high temperature solid state reaction route. For the ferroelectric characterization and non-volatile memory effect, 100 kHz thermal hysteresis loops were observed by Sawyer-Tower circuit. The electrical properties, I-V tracing was measured and low voltage resistance (LVR), maximum diode current (I_{max}) and threshold voltage (V_{TH}) were studied. From ln I-V linear relationship, ideality factor (η) and zero- bias voltage barrier high (ϕ_{bo}) were calculated. The C-V tracing was studied at 100 kHz under biased voltage from -4 V to 4 V. From the detail analysis, PTA6 layer on Si is quite acceptable for single capacitor (1C) of non-volatile ferroelectric random access memory device applications.

Keywords_ Ferroelectric, ideality factor (η), non-volatile, PTA6, perovskite

1 INTRODUCTION

INNOVATION in modern information technology are critically dependent on the development of denser, faster and less energy-consuming nonvolatile memories (NVMs). Ferroelectric random access memories (FRAMs) are considered to be ideal memory devices because of their novolatile property, low operation voltage, larger storage capacity and fast read/write speed characteristics [1].

For last decades ferroelectric materials are being considered for application in different kinds of devices, such as storage information and photonic devices, piezoelectric actuators and infrared sensors. Utilization of ferroelectrics in the form of thin films is even more attractive since it allows their integration into existent semiconductor circuit technology and certain of new types of the devices [2].

Ferroelectricity is a spontaneous electric polarization of a material that can be reversed by the application of an external electric field. The spontaneous polarization of ferroelectric materials implies a hysteresis effect which can be used as a memory function, and ferroelectric capacitors are indeed used to make ferroelectric RAM for computers [3].

Modified lead titanate compositions have recently been tested in the form of thin films aiming at applications such as nonvolatile memories, surface acoustic wave, delay line, pyroelectric sensors, optical shutters and modulators. Their piezoelectric, electrooptic and pyroelectric properties have been proved to be interesting for such applications, if they can be prepared in perovskite structure [4].

However the degradation of ferroelectric properties with decreasing film thickness is a common problem of $PbTiO_3$ type ferroelectric thin films. This degradation is caused mainly by oxygen vacancies that diffused from the film surface through the grain boundaries during firing [5,6]. In order to improve the electric properties of the complex $PbTiO_3$ ceramics, a lot of elements have been doped. Zhaung et al have reported that Al substituted to Ti since the radius of Al^{3+} cat-ion is about the same as that of Ti^{4+} (130 pm~140 pm) and found that the Al doped $PbTiO_3$ thin films showed low leakage current as compared with $PbTiO_3$ thin films [7].

Today, ferroelectric memories are moving from the laboratory to the market place [8]. Non-volatile memory devices based on ferroelectricity are a promising approach toward the development of a low cost memory technology [9].

Structural and microstructural properties of Al (6 mol%) doped $PbTiO_3$ powder have been reported [10]. In this study, we reported the nonvolatile memory behaviour, current vs voltage characteristics and capacitance vs voltage characteristics of Al (6mol%) doped $PbTiO_3$ thin film devices.

2 EXPERIMENTAL PROCEDURE

To prepare the colloidal precursor solution, PbO, TiO_2 and Al_2O_3 were used as starting materials. The purity of materials was 99.9% as analar grade. Each chemical was ground in agate mortar for 3 h to form homogeneous grain size. To reduce the grain size, the powder was sieved with 3-stages mesh sieve (100 mesh, 250 mesh and 400 mesh). Then this sample powder was dispersed by the air-jet milling under the pressure of 40 lb/in^2 to obtain the moisture less particle and blander for 15 min with constant pressure to ensure good dispersion. And then the powder was ground by ball-milling in 20 h. Then they were mixed to get the chemical formula $PbTi_{(1-x)}Al_xO_3$ (x=0.06 mol). And then it was heated at 800°C and 900 °C for 1 h. The PTA powder (900 °C) was chosen for further investigation because of its smaller crystallite size. Al doped $PbTiO_3$ were weighed and dissolved in 2 methoxyethanol solvent. The

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mixture solution was acidified with 3 mg of HCl. The solution was stirred and refluxed to form precursor solution.

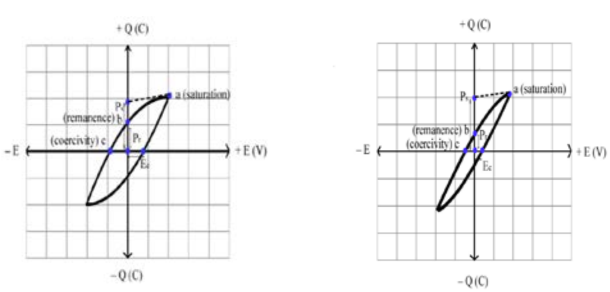
The substrate used for this study was p-Si (100), which were (0.5 cm×1 cm) and thickness of 280-300 μm. Before film fabrication, they were washed in distilled water. Then they were washed in boiling acetone and in boiled propenol for 5 min to remove greasy films. And then they were immersed in nitric acid for 5 min in order to remove ionic contamination. After that they were etched in buffered hydrofluoric acid for 5 min to remove oxide films. Finally the Si wafers were cleaned in distilled water and dried on flat oven at 100 ˚C in open air for a few minutes then the clean Si wafers were obtained.

The PTA6 precursor solution was spin-coated onto polished p-Si (100) substrates for 30 min each. The five process temperatures 500 °C, 550 °C, 600 °C, 650 °C and 700 °C were also performed according to examine the PTA film quality

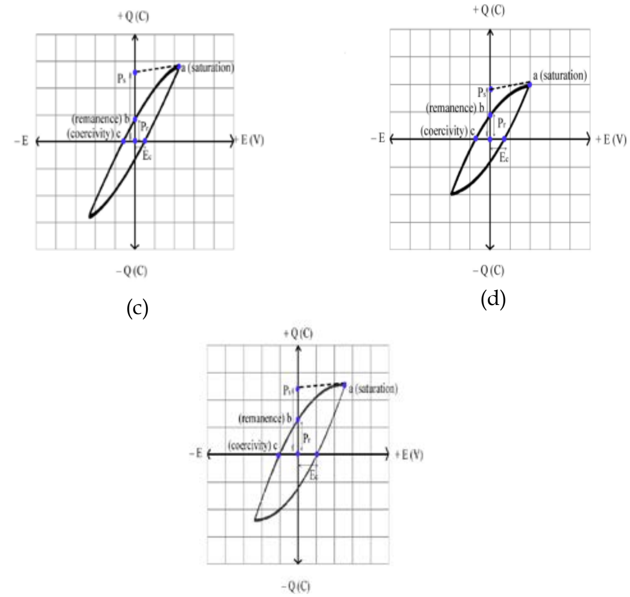
3 RESULTS AND DISCUSSION

3.1 Thermal Hysteresis Characteristics (Non- volatile Memory)

If we first applied a small electric field, we will have only a linear relationship between electric field strength increased. Then a field strength decreased, the polarization would be generally decreased, but did not return back to zero. When the field was reduced to zero, the crystal would exhibit a remanent polarization (P_r). The extrapolation of the linear segment of the curve back to the polarization axis represented the value of the spontaneous polarization (P_s). The strength of the field required to reduce the polarization P to zero was called the coercive field strength (E_c) [11].Ferroelectricity and nonvolatility of fabricated PTA6 films were interpreted by means of P-E hysteresis loop. Hysteresis loop measurements were performed with Sawyer- Tower circuit at applied frequency 100 kHz and device voltage of 10 V. PTA6 sample was served as circuit element and the loop was recorded on oscilloscope (YOKOGAWA ALSIO 50 MHz). Figure 1 (a-e) described the thermal hysteresis loop of metal ferroelectric semiconductor (MFS cell) with PTA6 film. All hysteresis loops were quite acceptable and exhibital three complete points such as saturation, remanence and coercivity. All measurable hysteresis parameters were quoted in Table 1. From the view point of digital electronics, PTA6 films could be used as a prototype of non-volatile memory applications.



(a) (b)



(c) (d)

(e)

Fig 1. Thermal hystersis loop of MFS cell with PTA6 film at (a) 500°C , (b)550°C, (c) 600°C , (d) 650°C and (e) 700°C

TABLE 1
HYSTERESIS PARAMETER FOR PTA6 FILMS AT DIFFERENT TEMPERATURES

Process Temperature(°C)	P_s(μC cm^{-2})	P_r(μC cm^{-2})	E_c(kVcm^{-1})
500	14.3	3.25	6.9
550	13.0	3.64	7.7
600	13.5	3.38	6.6
650	14.6	7.28	13.8
700	14.1	3.38	6.6

3.2 Current-Voltage Characteristics

To investigate the processing condition for preparation of the PTA6 thin film on p-Si (100) substrates by colloidal precursor deposition method and their electrical properties were examined.

In this study, the forward bias characteristic of the device was determined but not for the reverse bias because of the negligible amount of reverse bias current was present. The I-V characteristic was studied not only to provide guidelines for using them of device characterization but also establish an improved decision to account for electrical behaviours of Schottky-like ferroelectric memory diode. I - V tracing was observed to examine the leakage current in the film. The voltage applied to the copper electrode was defined as positive for the p-Si substrate to perform on the accumulation region so that there were no depletion region in the substrate. To eliminate the transient response the current measurement was carried out at the step voltage, 0.2 V and delay time, 2 min. The I - V characteristics were shown in figure 2. As it was seen from this figure, all I-V graphs were similar on variation nature. The current flow through the PTA6 memory diode was exponentially enhanced with an increase in voltage drop across the Cu-contact set with PTA6 film. Asymmetric I-V curve was

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said to be formed as two distinct states in forward region. These values were found to be calculated from the linear part in forward region. These values were 13.513Ω, 20.001Ω, 23.809Ω, 27.770Ω and 40.001Ω for respective cell. The wider dead-space was formed when the processing temperature was increased. The threshold voltages were 2.0V, 2.3V, 2.4V, 2.5V and 3.0V for fabricated memory diode up to 500°C, 550°C, 600°C , 650°C and 700°C respectively. These values were collected and listed in Table 2.

ln I-V response was essentially observed to identify the diode parameters such as ideality factor and zero-bias barrier height. These ln I-V plots were shown in figure 3. For calculation of diode parameters, we used the following equation.

$$I = I_s \exp(\frac{qV}{\eta KT}) \quad (1)$$

Where V is the applied voltage drop across the semiconductor surface depletion layer. Further, η is ideality factor, K is the Boltzmann constant, T is the temperature, q is the electronic charge and I_s is the saturation current, which is expressed by

$$I_s = AR^* T^2 \exp(\frac{q\phi_{bo}}{KT}) \quad (2)$$

Where A is the diode area, R* is the Richardson constant (8.16 $AK^{-2}cm^{-2}$), ϕ_{bo} is the zero-bias barrier height. Using (1), the value of the ideality factor (η) of diode at different temperatures were calculated. ϕ_{bo} had been determined from the extrapolated experimental saturation current was using (2) . The resulting values were quoted in Table 2.

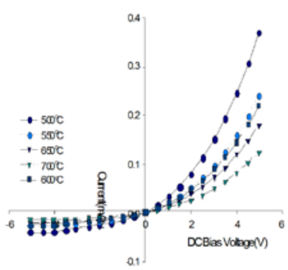


Fig 2. I-V characteristics of PTA6 thin films

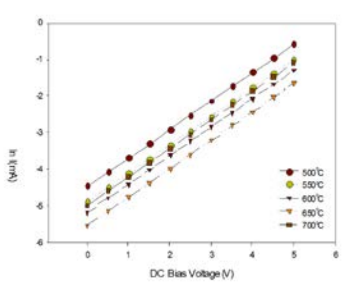


Fig 3. ln I-V characteristics of PTA6 thin films

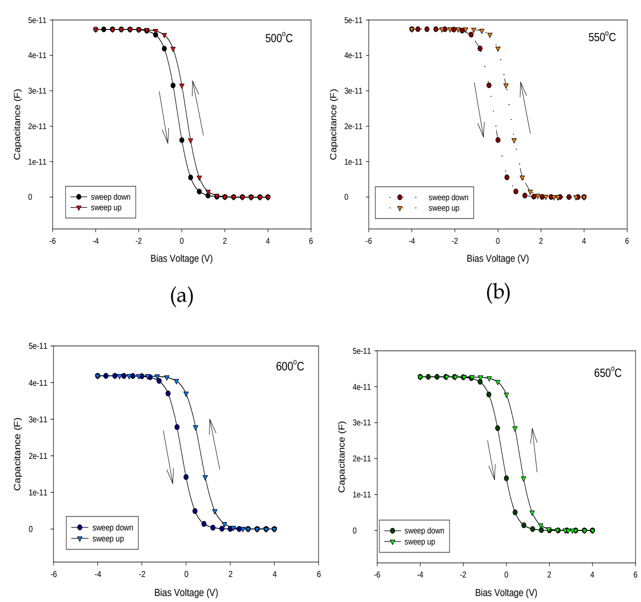
TABLE 2.

LVR, I_{max}, V_{TH}, η AND ϕ_{bo} OF THE PTA6 THIN FILMS

Process Temperature(°C)	LVR (kΩ)	I_{max} (mA)	V_{TH} (V)	η	ϕ_{bo}(eV)
500	13.51	0.37	2.00	1.42	0.29
550	20.00	0.25	2.30	1.63	0.39
600	23.81	0.21	2.40	1.64	0.39
650	27.77	0.18	2.50	1.65	0.39
700	40.00	0.13	3.00	1.67	0.40

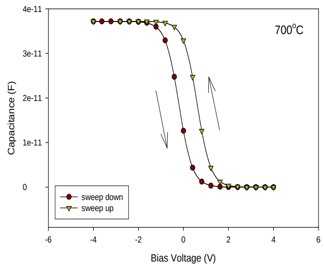
3.3. Capacitance -Voltage Characteristics Measurement

The voltage dependence of the capacitance was measured using the low pass RC circuit as an integrator at 100 kHz square pulse at room temperature. Voltage defined as having a positive polarity when a positive bias voltage was applied to the top electrode Cu. Figure 4 (a-e) showed the capacitance-voltage (C-V) characteristics in the region of -4 V to 4 V at 100 kHz. The voltage applied at the top metal was swept up for -4 V to 4 V and the back from 4 V to -4 V. The PTA6 films on Si substrates, the memory window of the hysteresis were about 1.3 V, 1.4 V, 1.45 V, 1.46 V and 1.47 V under the bias condition. It clearly showed the regions of accumulation, depletion and inversion. It is important that the C-V curve went anticlockwise, which means that ferroelectric hysteresis of the PTA6 film had controlled the Si surface potential and showed a memory effect due to polarization. We confirmed that Cu/PTA6/p-Si (MFS) structure give a larger memory window with increasing the process temperatures.



(a) (b)

(c) (b)



(e)

Fig 4. Capacitance versus bias voltage characteristics at (a) 500°C,(b)550°C,(c)600°C,(d)650°C and (e)700°C

4. CONCLUSION

Chemically derived $PbTi_{0.94}Al_{0.06}O_3$ (PTA6) thin layer was formed on P-Si (100) substrate at different process temperatures. Ferroelectricity and nonvolatility of PTA6 films were analyzed by mean of P-E hysteresis loop. All generated loops were acceptable and measured hysteresis parameters were quite feasible. From the hysteresis loop measurements, Al doped $PbTiO_3$ films can be used as single capacitor (1C) of NVFRAM (non-volatile ferroelectric random access memory). I - V characterization showed the rectification effect . The forward bias to the Cu/Ferroelectric lead-based titanate thin films and this forward part of the curve could be explained Al modified lead-based titanate films were p-type conductivity. In the case of PTA, the zero bias barrier height would increase as the temperature was increased. The memory window estimated from capacitance and voltage characterization measurement, it was clearly suggested that the influence of process temperature due to the wider value of window.

Thus the present research allowed more economical coating, technical simplicity and easy adaptability. Moreover, the films fabricated with sol-based method were quite promising candidate for memory device applications.

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