BEHAVIOR AND FERROELECTRIC PROPERTIES OF LEAD TITANATE FILMS AS A GATE MATERIAL

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Abstract

$PbTiO_3$: Sr thin film devices are prepared by colloidal solution route at different Sr contents. Structural features of prepared samples are examined with the help of x - rays diffraction technique. From the x - rays spectra, lattice dimensions, such as lattice constants, lattice distortion, unit cell volume, crystallite size and lattice micro strain of prepared samples at different Sr contents are evaluated. It is obvious that, there are single phase, tetragonal, polycrystalline and perovskite - type $PbTiO_3$ structure in prepared samples. FET behavior, known as drain and transfer characteristics of prepared samples are also studied. From the drain characteristic, operation of prepared samples is either enhancement mode or depletion mode is determined. It is obtained that; operations of prepared samples are enhancement mode and normally off nature. Maximum drain current threshold voltage and transconductance values are estimated from the transfer variations. Ferroelectric properties of prepared samples are characterized by using Sawyer - Tower circuit and ferroelectric parameters are investigated. It is known that, ferroelectric parameters (P_s, P_r and E_c) increase as Sr content increases in prepared samples. It might be due to strengthing of second order hybridization, caused by isovalent Sr^{2+} ions in prepared samples. It may be conclude that, our prepared samples are suitable for one transistor (1T) of FeRAM application.

Keywords: $PbTiO_3$, isovalent Sr ions, XRD, FET, ferroelectricity

Introduction

Ferroelectric materials exhibit a spontaneous polarization in the absence of external electric field. This polarization can be reoriented by ion displacement in the crystal and polarization can be triggered by an external electric field, such that ferroelectric materials can have two electrically - controllable non - volatile states [Miller L. S. and McWhorter P. J., 1992: Sakai S., 2006]. As a result, ferroelectric random access memory (FeRAM) has long been studied as a non - volatile technology [Ishikawa H., 2001]. In a ferroelectric field effect transistor (FeFET), a ferroelectric insulator is employed as a gate insulator in a metal - oxide - semiconductor field effect transistor (MOSFET). It is known to be ferroelectric behavior is added to CMOS performance, while maintaining the back - bone of CMOS logic [Ishikawa H., 2012]. The channel conductance is used to detect the polarizarion state in the ferroelectric gate insulator, so data reading operation in FeFET is non - destructive. FeFET is a promising memory technology due to the fast switching speed in ferroelectric materials (nanosecond or less), its non - destructive readout, its non - volatile state and its simple structure for high density integration [Mikolajick T., *et al.*, 2018: Kim J. Y., *et al.*, 2021]. Lead titanate ($PbTiO_3$: PT), known as fundamental ferroelectric perovskite, has been constant interest because of its piezoelectric and pyroelectric properties, and high spontaneous polarization, and relatively small permittuy [Wang D. G., *et al.*, 2008: Bhatti H. S., *et al.*, 2016]. PT can accept considerable substitution in one or both cations site, while maintaining its original crystal structure. Partial replacement of cation site(s) with foreign metal ions, can modify the its already reported that, substitutions of isovalent ions, Ca^{2+}, Ba^{2+}, Sr^{2+} and Cd^{2+} into Pb site exhibit the strong ferroelectric behavior, while maintaining its perovskite crystal structure in PT [Pratiksha Devi *et al.*, 2012]. In this study, isovalent Sr^{2+} ions are chosen as a substitutent for doping owing to the fact that, ionic radius of Sr^{2+} ions (113 pm) is slightly smaller than Pb^{2+} ions (119 pm). It is also expected that isovalent Sr^{2+} ions can be easily incorporated into Pb site in host $PbTiO_3$ crystal [Jian M. and Katiyar R. S. 2002: Mesquita W. D., *et al.*, 2022: Pontes F. M., 2003]. Effect of isovalent Sr^{2+} ions doping

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on structural features, FET behavior and ferroelectric properties of $PbTiO_3$ gate material, prepared by colloidal precursor solution method is examined in this research work.

Experimental Procedure

2.1 Sample Preparation

To prepare isoalent Sr^{2+} ions doped $PbTiO_3$ colloidal precursor solution, commercial grade PbO, TiO_2 and SrO were used as starting precursors. Firstly, there precursors were weighted and mixed, according to following stoichiometric compositions: $Pb_{(1-x)} Sr_{(x)} TiO_3$, where x = 0.05, 0.10, 0.15, 0.20 and 0.25 respectively. The mixed precursors were grinded by ball - milling process for each 3 hrs. And then, the mixed precursors were conventionally sintered at 700 C° for each 3 hrs. Solid state sintering meant the bonding and densification of particles by the application of heat below the melting point of a material. During the sintering, the free surface area of the compact decreased, and it was normally accompanied with an increase of the density. After first sintering, the mixed precursors were grinded again for each 3 hrs. Then, the mixed precursors were sintered for each 3 hrs. After second sintering, the mixed precursors were dissolved in 2 - methoxyetanol ($CH_3COCH_2CH_2OH$) solvent. The mixed solutions were heated and stirred with water batch, known as indirect heat treatment, for each 2 hrs. The p - Si (111) wafers with dimension (1.5 cm x 1 cm x 125 μm) were used as substrates. Before deposition process, Si substates were cleaned by using standard semiconductor cleaning procedure. An insulating layer, silicon dioxide SiO_2, were thermally deposited on Si substrates. An insulating layer SiO_2 between ferroelectric $PbTiO_3$: Sr and Si, could reduce the intermixing problem. It could also minimize the effect of charge injection and weaken the electric field across the ferroelectrics. The middle zone of SiO_2/Si structures were covered with apezone wax, and the remaining two - end zones were etched with HF: DI with the ratio of 1: 3, to remove the insulating layers. To create the source (S) and drain (D) regions, n - type phosphorus was deposited on these two - end regions, and sintered at 600^oC for 2 hr. The source (S) and drain (D) regions were formed at two - end regions by diffusion mechanism. Further, isovalent Sr^{2+} doped lead titanate ($PbTiO_3$: Sr) colloidal precursor solutions were deposited onto middle zone of SiO_2/Si structure with the help of spin coating technique with 45 rpm in the clean chamber. Wet films were thermally dried at ambient temperature and sintered at 600^oC for each 2 hrs. Silver pastes with diameter 3 mm were formed onto these three regions source (S), drain (D) and gate (G). Three copper wires were attached to these regions as electrodes.

2.2 XRD Measurements

XRD studies were used to determine the phase formation, structural features and lattice dimensions of prepared samples by meant of Rigaku Multiflux x - rays diffractometer with Cu K_α ($\lambda = 1.5418$ Å) monochromatic radiation The prepared samples, known as $PbTiO_3$: Sr films were scanned in the 2θ range from $10°$ to $70°$ with a scanned speed of $0.01°$/sec. Applied voltage and current of x - rays generator were set to be 50 kV and 40 mA. From the x - rays spectra, variations of Sr content with lattice dimensions, such as lattice constants " a " and " c ", lattice distortion (c/a), unit cell volume, crystallite size and lattice micro strain were examined in $PbTiO_3$: Sr films.

2.3 FET Characteristic Measurements

For drain and transfer characteristic measurements, two power supplies (model abc) and two digital multimeters (model xyz) were used. Measurements were carried out in the DC voltage range from 0 V to 10 V, both for drain to source voltage (V_{ds}) and gate to source voltage (V_{gs}).

Further, to eliminate the transient responses, step voltage and delay time were set to be 0.1 V and 1 min. I (V) data were recorded manually. From the I (V) data, drain and transfer variations were studied.

2.4 Ferroelectric Characteristic Measurements

Ferroelectric behavior of the prepared samples was examined with the help of Sawyer - Tower circuit.

Results and Discussion

3.1 XRD Studies
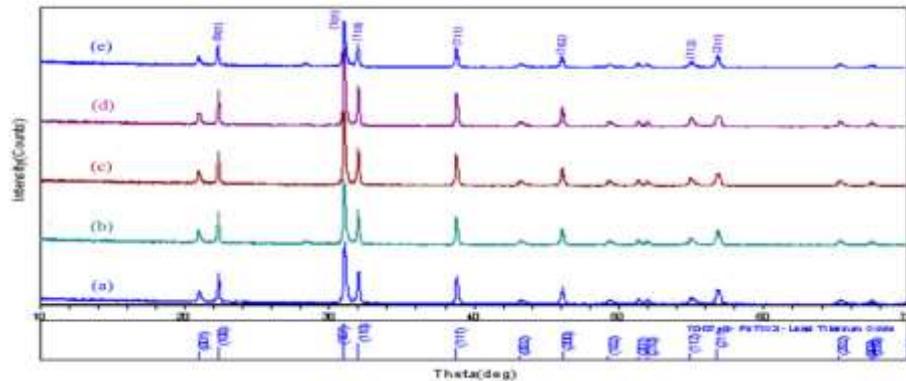
Figure1 XRD Spectra of $PbTiO_3$: Sr Films (a) Sr = 5 mol %, (b) Sr = 10 mol %,

(c) Sr = 15 mol % (d) Sr = 20 mol % and (e) Sr = 25 mol %

Figure (1) depicted the x - rays diffraction spectra of $PbTiO_3$: Sr films. Peak search algorithm (Jade Software) was used to identify the all unknown peaks in this research work. Only diffraction peaks from tetragonal, single phase, polycrystalline, perovskite - type $PbTiO_3$ structure with reference (70 - 0746 > JCPDS file no.) were observed. In addition, the most intense peak was (101) peak and a little shift of (101) peak (in term of 2θ value) was obtained in all x - rays spectra. It was also noticed that, there were no considerable change of tetragonal - phase $PbTiO_3$ structure after Sr doping. It was reported that, tetragonal to cubic phase transition, known as structural phase evolution was x = 0.50 by XRD technique in Sr doped $PbTiO_3$ films. However, FT Raman scattering revealed that tetragonal to cubic structural phase transition was x = 0.58. This contradiction could be explained by the fact that, Raman scattering probed short - range structural order, while XRD probed long - range structural order [Pontes F. M., 2003]. These results indicated that additional isovalent Sr^{2+} ions were easily incorporated into Pb - site in host $PbTiO_3$ lattice. From the x - rays spectra, lattice constants " a " and " c " of $PbTiO_3$: Sr films were evaluated by substituting interplanar spacing " d " values of (101) and (110) peaks in the following equation (1).

$$\frac{1}{d^2} \; = \; \frac{h^2+k^2}{a^2} + \frac{l^2}{c^2} \qquad\qquad (1)$$

$$d \quad = \text{interplanar spacing}$$

$$h, k, l = \quad \text{miller indices}$$

$$a, c \quad = \text{lattice parameters}$$

Interplanar spacing of 'd' values (101) and (110) peaks were substituted in equation (1) and lattice parameters 'a, c were estimated. Unit cell volume of $PbTiO_3$: Sr films were determined by using following equation (2) :

$$\text{tetragonal cell volume} = a \times a \times c \qquad (2)$$

where a, c = lattice parameters,

Unit cell volumes of the $PbTiO_3$: Sr films were examined by using the following equation (2). Lattice constants " a " and " c ", lattice distortion (c/a) and unit cell volume of $PbTiO_3$: Sr films were collected and listed in table (1)

Table 1 List of lattice constants, lattice distortion and unit cell volume of PbTiO3: Sr films.

Sr Content (%)	Lattice Parameter "a (Å)"	Lattice Parameter "c (Å)"	Lattice Distortion (/a)	Cell Volume ($\times 10^{-30} m^3$)
5	3.871	4.092	1.057	61.317
10	3.879	4.077	1.051	61.345
15	3.886	4.065	1.046	61.386
20	3.893	4.053	1.041	61.425
25	3.898	4.045	1.038	61.461

Crystallite size and lattice micro strain of $PbTiO_3$: Sr films were calculated by using the following Debye - Scherrer equations (3) and (4).

$$D = \frac{0.9\,\lambda}{\beta \cos\theta} \qquad (3)$$

$$\varepsilon = \frac{\beta}{4\tan\theta} \qquad (4)$$

In the above two equations, β is the full width at half maximum (FWHM) of the most intense peak (101), λ is the wavelength of the using x - rays, θ is the peak position of the (101) peak, known as Bragg's peak. Crystallite size, lattice micro strain and FWHM of the most intense peak (101) were collected and listed in table (2).

Table 2 List of crystallite size, lattice micro strain and FWHM of (101) peak, of PbTiO₃: Sr films.

Sr Content (%)	Crystallize Size (nm)	Micro Strain ($\times 10^{-3}$)	FWHM of (101) Plane (Rad) ($\times 10^{-3}$)
5	29.54	4.259	4.884
10	29.18	4.311	4.949
15	29.73	4.379	5.022
20	28.36	4.436	5.087
25	28.07	4.482	5.140

It was studied that, lattice constant " a ", unit cell volume, FWHM of (101) peak, and lattice micro strain increased as Sr content increased in $PbTiO_3$: Sr films. However, lattice constant " c ", lattice distortion (c/a) and crystallite size were lowered, as listed in tables (1 & 2). In $PbTiO_3$: Sr films, lattice distortion c/a was ~ 1.06, that caused the micro strain during the doping mechanism.

Further, there might be large lattice mismatch between $PbTiO_3$: Sr film and SiO_2/Si structure. Therefore, SiO_2/Si structure induced the lattice micro strain in $PbTiO_3$: Sr films. In addition, dislocation density was inversely proportional to the square of crystallite size. These results could be interpreted as the small variation of lattice dimensions in $PbTiO_3$: Sr films after Sr doping.

3.2 FET Studies

3.2.1 Drain Characteristic

Drain characteristic, known as I_{ds} - V_{ds} variations at different gate to source voltage (V_{gs}), were displayed in figure 2 (a ~ e).
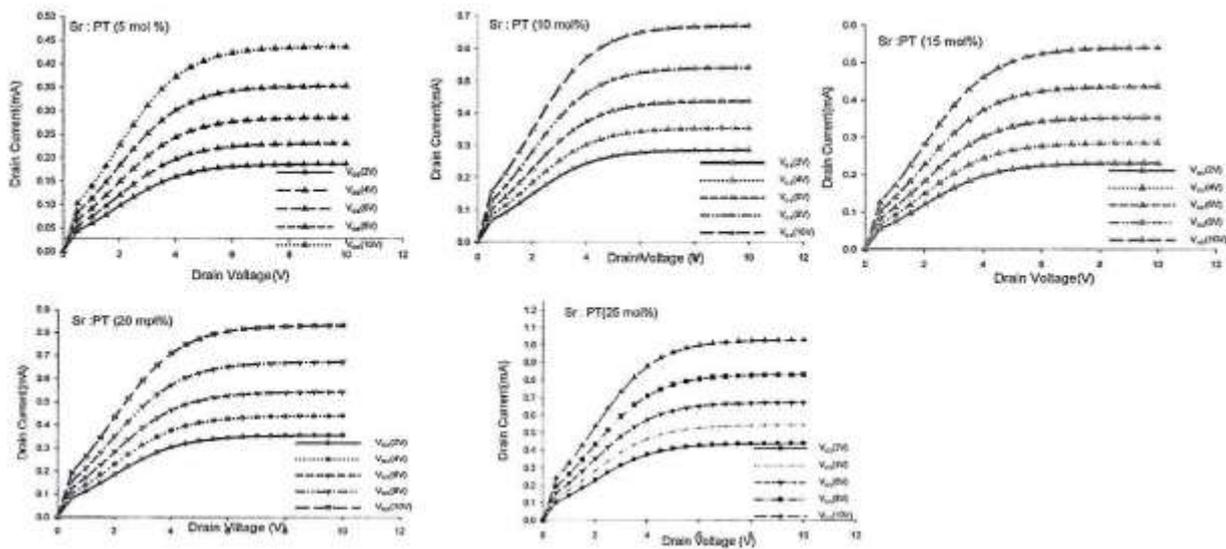
Figure. 2 Drain Characteristic of FET with $PbTiO_3$: Sr Gate Materials (a) Sr = 5 mol %,

(b) Sr = 10 mol %, (c) Sr = 15 mol % , (d) Sr = 20 mol % and (e) Sr = 25 mol %.

From these variations, two regions, linear and saturation were observed. At low drain to source voltage, between 0 V to 4 V, the drain current (I_{ds}) linearly increased when the drain to source voltage (V_{ds}) was raised. In this region, FET with $PbTiO_3$:Sr gate materials, exhibited the resistive characteristic, and as a function of gate to source voltage (V_{gs}). Further, drain to source current (I_{ds}) saturated at pin - off point and I_{ds} - V_{ds} variations saturated. Moreover, drain current (I_{ds}) was enhanced when the gate to source voltage (V_{gs}) was raised. It might be due to FET with $PbTiO_3$: Sr gate materials exhibited enhancement mode operation. In addition, the drain to source current (I_{ds}) was zero, when zero - bias gate - source voltage (V_{gs}) was applied. It was very similar to normally off nature of FET.

3.2.2 Transfer Characteristic

Transfer characteristic, known as I_{ds} - V_{gs} variations were studied at saturation mode and illustrated in figure 3 (a ~ e).
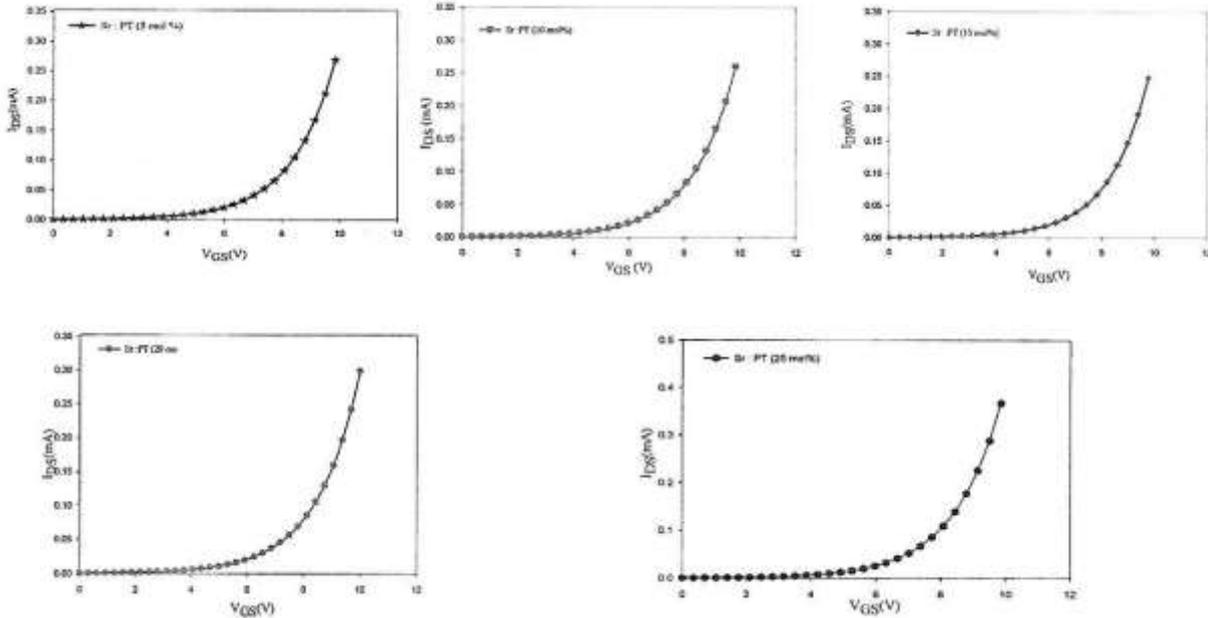
Figure 3 Transfer Characteristic of FET with PbTiO$_3$: Sr Gate Materials (a) Sr = 5 mol %, (b) Sr = 10 mol %, (c) Sr = 15 mol % ,(d) Sr = 20 mol % and (e) Sr = 25 mol %.

From these variations, it was obvious that, drain to source current (I_{ds}) increased exponentially with increasing gate to source voltage (V_{gs}). Further, threshold voltage (V_{th}) and maximum drain current (I_{dmax}) varied with Sr content in all transfer variations. To examine the parabolic nature of transfer variation, known as I_{ds} vs. (V_{gs} - V_{th}) variation, mth power of (Vgs - V_{th}) was studied by substituting the experimental data, such as V_{gs}, V_{th} and I_{ds} in equation (5), and mth power values for different Sr content in FET with PbTiO$_3$: Sr gate materials could be obtained.

$$I_{ds} = K. (V_{gs} - V_{th})^m \tag{5}$$

where I_{ds} = drain to source current

　K = constant

　V_{gs} = gate to source voltage, and

　V_{th} = threshold voltage

To examine the transconductance value of fabricated FET, $I_{ds}^{(1/m)}$ vs. V_{gs} variations were plotted and shown in figure 5 (a ~ e). From these variations, it was noticed that, $I_{ds}^{(1/m)}$ was linearly enhanced with increasing gate to source voltage (Vgs). The transconductance value (g_m) value was examined by the equation.

$$g_m = \frac{\delta I_d}{\delta V_{gs}} \tag{6}$$
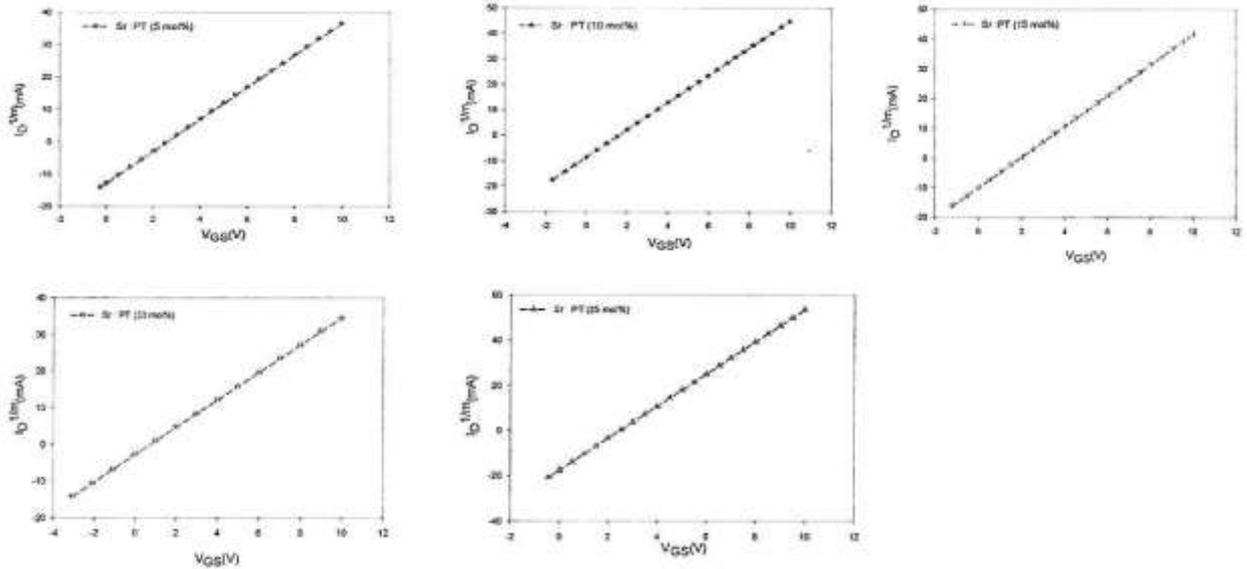
Figure 4 Transconductance Variations of FET with PbTiO$_3$: Sr Gate Materials (a) Sr = 5 mol %, (b) Sr = 10 mol %, (c) Sr =15 mol %, (d) Sr = 20 mol % and (e) Sr = 25 mol %.

Threshold voltage (V_{th}), maximum drain current (I_{dmax}), mth power and transconductance value (g_m) at different Sr content in fabricated FET with PbTiO$_3$: Sr gate materials were collected and listed in table (3).

Table 3 List of Threshold Voltage, Maximum Drain Current, mth Power and Transconductance Value at Different Sr Content in Fabricated FET.

Sr Content mol (%)	V_{th} (V)	I_{dmax}(mA)	$g_{m\ (mS)}$	mth power
5	3.46	192.65	4.87	2.05
10	2.84	191.18	6.61	1.94
15	2.82	190.48	10.36	2.07
20	2.74	190.13	5.28	2.09
25	2.72	190.00	3.81	1.98

3.3 Ferroelectric Studies

Ferroelectricity or non - volatity of prepared FET with PbTiO3: Sr gate materials, was characterized by using Sawyer - Tower circuit, by meant of its electric polarization vs. electric field characteristic, as depicted in figure 5 (a ~ b).
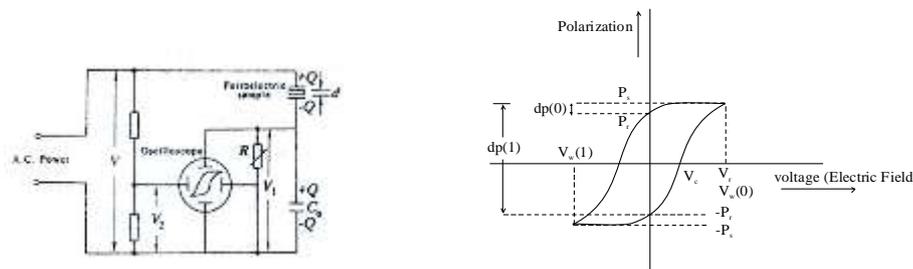
Figure. 5 (a) Sawyer - Tower Circuit (b) Estimation of Ferroelectric Parameters Ps, Pr and Ec.

Ferroelectric hysteresis loops were displayed in figure 6 (a ~ e). From these variations, it was noticed that, $I_{ds}^{(1/m)}$ was linearly enhanced with increasing gate to source voltage (Vgs). The transconductance value (g_m) value was examined by the equation.
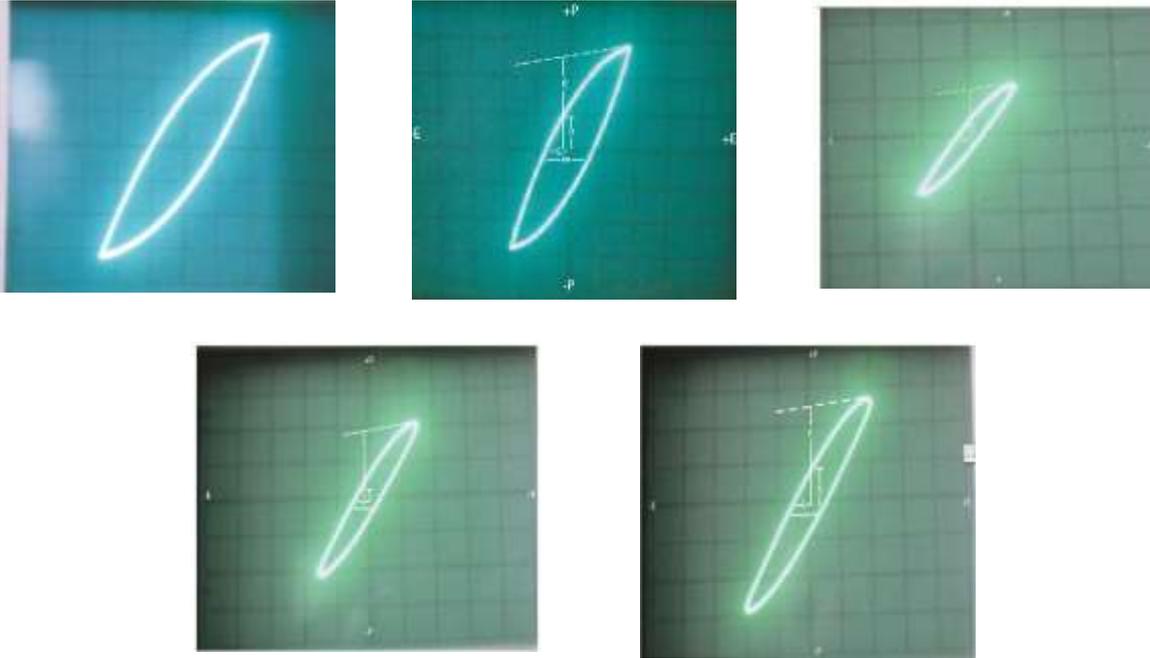
Figure 6 Ferroelectric Hysteresis Loops of $PbTiO_3$: Sr Gate Materials (a) Sr = 5 mol %,
(b) Sr = 10 mol %, (c) Sr = 15 mol %, (d) Sr = 20 mol % and (e) Sr =25 mol %.

Ferroelectric Parameters were listed in table (4).

Table (4) Ferroelectric properties P_s, P_r and E_c of prepared FET with $PbTiO_3$: Srgate materials.

Ba Content (%)	Spontaneous polarization $P_s(\mu C\text{-}cm^{-2})$	Remanent polarization $P_r(\mu C\text{-}cm^{-2})$	Coercive field E_c (kV cm^{-1})
5	11.4	2.4	3.6
10	11.6	2.6	3.9
15	11.9	2.8	4.1
20	12.2	3.1	4.3
25	12.6	3.4	4.6

It was obvious that, ferroelectric properties, such as Ps, Pr and Ec increased when the Sr dopant concentration was raised in prepared FET with $PbTiO_3$: Sr gate materials. It might be due to strengthing of second - order hybridization, caused by isovalent Sr^{2+} ions in $PbTiO_3$ lattice [Cohen R. E. and Krakauer H., 1992 : Turik A. V. and Khasabov A. G., 2000]. According to the experimental data, it is expected that our fabricated FET with $PbTiO_3$: Sr gate materials are suitable for ferroelectric field effect transistor (1 T) application.

Conclusion

Colloidal precursor solution derived FETs with ferroelectric $PbTiO_3$: Sr gate materials with different Sr content, are studied by means of its structural features, FET behavior and ferroelectric properties. XRD results reveal that, there are small variations of lattice dimensions with Sr contents, due to doping mechanism and large lattice mismatch between SiO_2/Si structures and PbTiO3: Sr films. However, there are no considerable change of tetragonal phase, perovskite - type $PbTiO_3$ structure after Sr dopings. FET results can be interpreted as our fabricated FETs exhibit enhancement mode operation and normally off nature, known as n - channel enhancement - mode MOSFET behavior. Ferroelectric properties of our fabricated FET indicate that, ferroelectric parameters, such as Ps, P_r and E_c increase as Sr dopant increases in our fabricated FET. It may be due to strengthing of second - order hybridization, caused by isovalent Sr^{2+} ions in $PbTiO_3$: Sr gate materials. It can be concluded that, our fabricate FETs with ferroelectric $PbTiO_3$: Sr gate materials are suitable for one transistor (1 T) in ferroelectric random access memory (FeRAM) applications.

Acknowledgements

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