Chapter- 4

Device Characteristics of CSD Grown $Y_{0.95}Ca_{0.05}MnO_3/Si$ Thin film
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4.1. Introduction:

Continuous search for faster, smaller, cheaper and power efficient devices encouraged physicists and materials scientists to work on few functional oxide materials such as mixed valent manganites, multiferroics, diluted magnetic semiconductors (DMS), etc. Increasing attention has been focused on mixed valent manganites due to their interesting interrelated properties, phase coexistence and phase separation scenario. Since last two decades, manganites are studied in the form of polycrystalline bulk [1], nanostructure [2], thin film [3], device [4], multilayer [5], heterostructure [6], composite [7], etc for various applications such as temperature sensor [8], magnetic field sensor [9], p-n junction [10], field effect device [11], etc. In manganites, four fundamental parameters – spin, charge, lattice and orbital – are strongly coupled resulting in different ground states such as ferromagnetic metallic (FMM), ferromagnetic insulator (FMI), antiferromagnetic insulator (AFMI), paramagnetic metallic (PMM), paramagnetic insulator (PMI), etc. From fundamental point of view, manganites possess intrinsic disorder ensuing in the non-uniform system at nanoscale level [12, 13] and phase separation at micrometer scale [14]. Origin of magnetoresistance (MR) in manganites can be satisfactorily explained by phase separation and related phenomena. However, from the application view point, manganites should be studied for their potential device applications.

Several reports exist on the current – voltage (I – V) studies on p-n junction based thin films and devices consisting of manganites [4, 9 – 16]. Effect of swift heavy ion (SHI) irradiation on I – V characteristics of La_{0.6}Pr_{0.2}Sr_{0.2}MnO_{3} / SrNb_{0.002}Ti_{0.998}O_{3} devices and modifications in the interface barrier height have been studied [4]. Khachar et al [9 – 11] have reported I – V behavior of manganite based heterostructure and explored temperature and field dependent MR behavior of interface, positive MR and field effect studies. Jin et al [12] have investigated positive colossal magneto resistance (CMR) from interface effect in p-n junction of La_{0.9}Sr_{0.1}MnO_{3} and SrNb_{0.01}Ti_{0.99}O_{3}. Also, positive CMR effect has been observed in ZnO / La_{0.7}Sr_{0.3}MnO_{3} heterostructure which has been discussed in the context of field induced modifications in depletion layer and
capture carrier effect across the interface [13]. Hu et al [14] have studied magnetic field dependent I – V behavior of La$_{0.9}$Sr$_{0.1}$MnO$_3$ and SrNb$_{0.01}$Ti$_{0.99}$O$_3$ p-n junction at different temperatures. Temperature dependent rectifying I – V characteristics have been discussed on the basis of modifications in the thickness of depletion layer [15]. Thickness dependent I – V (T) characteristics of La$_{0.8}$Pr$_{0.2}$Sr$_{0.2}$MnO$_3$ / Nb-SrTiO$_3$ p-n junction based bilayered manganite devices have been investigated [16].

YMnO$_3$ is hexagonal ferroelectric manganite having ferroelectric transition (T$_{CE}$) ~ 1000K and antiferromagnetic transition (T$_{N}$) ~ 120K. Kitahata et al [17] have studied dielectric properties of YMnO$_3$ films grown by dip coating technique. Studies on dielectric and ferroelectric properties of sol-gel grown YMnO$_3$ films were reported [18, 19]. Moure et al [20] have reported non-ohmic behavior and switching phenomena in YMnO$_3$ based ceramic materials. Li et al [21] have fabricated epitaxial orthorhombic YMnO$_3$ thin films on (001) Nb:SrTiO$_3$ single crystal wafer using pulsed laser deposition (PLD) method and discussed I – V rectifying characteristics on the basis of the competition between thermal excitation and possible ferroelectricity. Yi et al [22] have studied temperature dependence of capacitance – voltage and current – voltage characteristics of highly oriented YMnO$_3$ / Si thin films.

Several thin film fabrication methods have been reported for growing high quality manganite films such as PLD, magnetron sputtering, molecular beam epitaxy (MBE), chemical vapor deposition (CVD), physical vapor deposition (PVD), sol-gel, dip coating, chemical solution deposition (CSD), etc. CSD is a simple and cost effective method for the growth of good quality homogeneous manganite films on suitable substrates. More importantly it is vacuum free technique of thin film deposition.

Keeping in mind all the above aspects of YMnO$_3$ manganite and CSD method, in this chapter, we report the results of the studies on device characteristics of CSD grown Y$_{0.95}$Ca$_{0.05}$MnO$_3$ manganite films grown on single crystalline (100) Si substrate. Temperature dependent current – voltage and capacitance – voltage characteristics have been discussed in the context of film – substrate interface modifications due to annealing of films at different temperatures.
4.2. Experimental Details:

$Y_{0.95}Ca_{0.05}MnO_3$ (YCMO) films were grown on single crystalline $(100)$ Si substrate using chemical solution deposition (CSD) technique under deposition conditions given as follows: Precursors: High purity yttrium acetate $[Y(CH_3CO_2)_3 \times XH_2O]$, calcium acetate $[Ca(CH_3CO_2)_2 \times 4H_2O]$ and manganese acetate $[Mn(CH_3COO)_2 \times XH_2O]$; Stoichiometry: $Y:Ca:Mn = 95:5:100$; Solution: 1:1 volume ratio of acetic acid and double distilled water; Molarity: 0.4M solution; Stirring: 90°C using magnetic stirrer until a clear and transparent solution was obtained; Spin Coating: On cleaned Si $(100)$ substrates by using spin coater; RPM: 4000rpm for 25sec; Heating: Prepared films were heated at 150°C for 30min in order to remove water content; Calcination: Heated films were calcined at 350°C for 30min in furnace to repel organics; Repetition: Above processes (from spin coating to calcination) were repeated twice to obtained ~ 140nm film thickness; Annealing: Annealed at 700°C and 900°C for 24hrs in O$_2$ environment.

Thickness of well annealed YCMO films was precisely measured using DekTak thickness profilometer and thickness was found to be ~ 136nm for YCMO film annealed at 700°C and ~ 139nm for 900°C. X-ray diffraction (XRD) measurements were carried out to understand the crystallographic structure of YCMO/Si films while surface morphology and magnetic topography were examined using atomic force microscopy (AFM) and magnetic force microscopy (MFM), respectively. Temperature dependent Current–voltage (I–V) and capacitance–voltage (C–V) were collected in the range 150–300K using two probe transport set–up with current perpendicular to plane (CPP) measurement geometry.

4.3. Structural Studies:

Figure 4.1 depicts typical XRD pattern of YCMO / Si film annealed at 900°C revealing $(h00)$ oriented growth of the film parallel to $(100)$ single crystalline Si substrate. Inset of figure 4.1 shows an enlarged view of $(100)$ peaks of the film and
substrate showing the separation between them signifying the presence of strain at the interface.

Strain can be calculated using the formula:

\[
\delta (%) = \left[ \frac{(d_{\text{substrate}} - d_{\text{film}})}{d_{\text{substrate}}} \right] \times 100.
\]

**Figure 4.1:** Typical XRD pattern of Y\(_{0.95}\)Ca\(_{0.05}\)MnO\(_3\) / Si film annealed at 900°C

It is found that value of \(\delta\) decreases from \(-1.13\%\) (in 700°C film) to \(-0.39\%\) (in 900°C film) which can be attributed to the higher annealing induced improved interface and suppression in lattice disorder at the interface in 900°C annealed film. In addition, it
is clearly seen in figure 4.1 that few peaks, addressed by appropriate \((hkl)\) indices, reveal the polycrystalline nature of YCMO / Si film having hexagonal structure.

### 4.4 Microstructural Studies:

![AFM images of Y\(_{0.95}Ca_{0.05}MnO_3\)/Si films annealed at 700°C](image)

**Figure 4.2:** (a) AFM images of \(Y_{0.95}Ca_{0.05}MnO_3\)/Si films annealed at 700°C
Figure 4.2: (c) & (d) MFM topographs of $Y_{0.95}Ca_{0.05}MnO_3 / Si$ films annealed at 700°C.

Figure 4.2: (b) AFM images of $Y_{0.95}Ca_{0.05}MnO_3 / Si$ films annealed at 900°C.
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Figure 4.2: (e) & (f) MFM topographs of Y$_{0.95}$Ca$_{0.05}$MnO$_3$/Si films annealed at 900°C.

Figure 4.2 shows the AFM micrographs of YCMO / Si films annealed at (a) 700°C and (b) 900°C. It is clearly seen that both the films possess island like grain growth with the grain size ~ 200nm (700°C) and ~ 240nm (900°C) and rms surface roughness ~ 17.27nm and ~ 12.43nm for 700 and 900°C annealed films, respectively. Higher grain size and smaller surface roughness in film annealed at higher temperature can be attributed to the agglomeration effect among the smaller grains and formation of sharp grain boundaries. Figure 4.2 also shows MFM micrographs obtained at lift height of (c) 30nm and (d) 60nm for 700°C annealed film and (e) 30nm and (f) 60nm for 900°C annealed film revealing the fact that with the change in lift height, contrast in the granular structure gets changed suggesting the magnetic response of the films.

4.5 Transport Properties:

To understand the transport properties of presently studied YCMO / Si films, I – V measurements were carried out at 150, 200, 250 and 300K by applying
voltage pulses in the voltage range: +5V to –5V and measuring the current across the junction under CPP mode. Figure 4.3 shows I – V curves collected at different temperatures (current is shown in logarithmic scale) for YCMO / Si films annealed at 700°C and 900°C. Asymmetry between the forward and reverse bias modes implies its potential for practical applications in spintronic based memory devices. In addition, it is clearly seen that with increase in temperature, current gets increased indicating semiconducting (or insulating) nature of both the junctions under study. Insets of figure 4.3 show the normal scale I – V characteristics of YCMO / Si films annealed at different temperatures depicting rectifying behavior throughout the temperature range studied. Increase in the slope of forward bias I – V (dI / dV) confirms the semiconducting behavior of the junctions (inset of figure 4.3). Small leakage current can be drawn across the junctions, as indicated by large ratio between $I_{\text{forward}} / I_{\text{reverse}} \sim 10^4$ at 300K which remains almost constant at all the temperatures studied.

While comparing both the junctions for their transport behavior, at 300K, current drawn across the junction annealed at 700°C is found to be larger as compared to 900°C, which can be understood as: structural strain for 700°C is –1.13% which is larger than –0.39% found for 900°C film indicating better transport in higher annealed film and hence large current can be drawn across the junction annealed at 900°C [4]. In addition, in 700°C, grain size is smaller ~ 200nm as compared to 900°C film (AFM micrographs) while rms surface roughness is larger resulting in the increased number of grain boundaries thereby scattering of charge carriers at the boundaries get enhanced and hence current is smaller in 700°C annealed film as compared to 900°C film. As shown in insets of figure 4.3, current remains almost invariant with applied voltage up a certain value, $V_d$, after which current increases sharply with voltage (indicated by arrow). $V_d$ signifies the energy required to transport the charge carriers (electrons) from Si to YCMO during forward bias mode.
Figure 4.3: Current – Voltage (I – V) characteristics (in logarithmic scale) recorded at different temperatures for $Y_{0.95}Ca_{0.05}MnO_3$ / Si films annealed at (a) 700°C and (b) 900°C. Insets: Temperature dependent I – V characteristics for both the junctions
It is found that $V_d$ shifts towards lower value with increase in temperature for both the junctions which can be ascribed to the thermally activated charge carriers crossing the interface. In higher annealed film, $V_d$ is smaller as compared to lower annealed film which is due to the sharp interface and smaller interfacial strain in 900°C annealed film.

To understand the possible mechanism responsible for the charge transport behavior in forward bias mode of presently observed $I - V$ characteristics, various reported mechanisms were used to fit the experimental $I - V$ data, including (i) Fowler–Nordheim (F–N) tunneling ($\ln \{I / V^2\} \text{ vs. } V^{-1}$), (ii) thermionic emission (T–E) mechanism ($\ln I \text{ vs. } V^{1/2}$), (iii) Poole–Frankel (P–F) emission mechanism ($\ln \{I / V\} \text{ vs. } V^{1/2}$) and (iv) space charge limited conduction (SCLC) mechanism ($I \alpha V^2$) [4, 11, 23]. To confirm an appropriate mechanism responsible for the presently obtained $I - V$ characteristics, experimental $I - V$ data collected at 300K for both the junctions have been fitted theoretically using above mechanisms as shown in figure 4.4. It is clearly seen that straight line fitted SCLC mechanism is obeyed nicely by the charge carrier transport across the junctions.

Figure 4.5 shows the straight line fits to experimental $I - V$ data collected at different temperatures for both the junctions under study using SCLC model of the form: $I_{\text{SCLC}} = 9\mu_e \varepsilon_0 \theta V^2 / 8d^3$; $I \alpha V^2$, where $d$ is the film thickness and $\theta$ is the ratio of free electron density to trapped electron density at the interface which is proportional to the slope of the $I \text{ vs. } V^2$ curve.

It is clearly seen that the straight line is fitted well to $I - V$ curves throughout the higher voltage range ($V > 1.5V$) with continuous increase in slope ($dI/dV^2$) with increasing temperature indicating an enhanced free to trapped electron density ratio ($\theta$) with temperature resulting into the large conduction across the junctions. While comparing both the junctions, $\theta$ is higher in higher annealed film which is mainly due to the sharp interface and lower interfacial structural strain in higher annealed film.
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Figure 4.4: Plots of (a) $\ln (I/V^2)$ vs. $V^{-1}$ [F–N tunneling model] (b) $\ln (I)$ vs. $V^{1/2}$ [T–E model] (c) $\ln (I/V)$ vs. $V^{1/2}$ [P–F emission model] and (d) $I$ vs. $V^2$ [SCLC mechanism model] for the I–V characteristics (forward bias mode) carried out at 300K for both the nanostructured $Y_{0.95}Ca_{0.05}MnO_3/Si$ films annealed at 700°C and 900°C
Figure 4.5: Forward biased I–V data linearly fitted to SCLC model at different temperatures for both the nanostructured $Y_{0.95}Ca_{0.05}MnO_3/Si$ films annealed at 700°C and 900°C
4.6 Rectifying Property:

![Graph showing rectifying ratio vs voltage for Y\textsubscript{0.95}Ca\textsubscript{0.05}MnO\textsubscript{3}/Si films annealed at 700°C and 900°C.]

**Figure 4.6:** Room temperature rectifying ratio obtained from I – V data for Y\textsubscript{0.95}Ca\textsubscript{0.05}MnO\textsubscript{3}/Si films annealed at 700°C and 900°C

Figure 4.6 shows the voltage dependent rectifying ratio (calculated by \(I_{\text{forward}} / I_{\text{reverse}}\), \(I_{\text{forward}}\) is the forward current and \(I_{\text{reverse}}\) is the reverse current) at 300K for presently studied junctions revealing that rectifying ratio increases with voltage up to 2.8V and then starts to decrease in 900°C annealed film while it continuously increases for lower annealed film. Also, value of maximum ratio is found to be \(~1.2 \times 10^4\) (@ 2.8V) in 900°C annealed film which becomes \(~2.2 \times 10^4\) (@ 4.9V) in lower annealed film. This can be due to the large leakage current across the junction annealed at higher temperature as compared to lower temperature annealed junction.
4.7 Sensing Property:

![Graph showing Applied electric field dependence of electroresistance (ER) at room temperature for Y_{0.95}Ca_{0.05}MnO_3/Si films annealed at 700°C and 900°C. Inset: Variation in junction resistance with applied electric field at 300K.](image)

Figure 4.7: Applied electric field dependence of electroresistance (ER) at room temperature for Y_{0.95}Ca_{0.05}MnO_3/Si films annealed at 700°C and 900°C. Inset: Variation in junction resistance with applied electric field at 300K.

Non-linear I – V curves observed for the presently studied junctions indicates an existence of electroresistance (ER) behavior across the junctions [24, 25]. Odagawa et al [25] have reported colossal electroresistance (CER) ~ 5000% in Pr_{0.7}Ca_{0.3}MnO_3 manganite based sandwiched structure. Khachar et al have reported small tunneling electroresistance (TER) ~ 19% at 300K across the manganite based p-n junction [10]. Also, room temperature voltage induced large ER ~ 2683% in manganite based heterostructure has been discussed in the context of modifications in the charge carrier.

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density and electronic states [6]. In order to understand the charge transport properties of presently studied junctions, electric field dependent junction resistance was measured at 300K for both the junctions. Inset of figure 4.7 shows the variation in junction resistance $J_R$ with applied electric field (E) measured at 300K for both the junctions showing large reverse bias resistance in the range of GΩ suggesting the better quality of the junctions. Junction resistance is larger in lower annealed film which may be due to the large number of grain boundaries and higher structural strain at the interface. Fluctuations in junction resistance in reverse bias mode may be attributed to the disorder and inhomogeneity at the interface and manganite layer [9, 26].

Figure 4.7 shows room temperature variation in ER [ER% = $(J_{R(E = E)} - J_{R(E = 0)}) / J_{R(E = 0)} \times 100$] with applied electric field for both the junctions under study. Both the junctions show large positive ER during reverse negative field cycle while positive electric field suppresses junction resistance resulting in negative ER $\sim$ 100%. Lower annealed junction exhibits large positive ER $\sim$ 600% while lower annealed junction exhibits positive ER $\sim$ 300%. For both the junctions, initially positive ER starts to increase and then remain almost constant while negative ER increases up to electric field of $\sim$ 70kV/cm after which it remains invariant with field. For lower annealed film, positive ER starts to decrease and becomes negative in sign well above 210kV/cm applied electric field. Complex variation in ER with applied electric field can be understood as: positive cycle of applied field pushes electrons from Si towards YCMO which cross the junction thereby increasing the carrier density at YCMO layer resulting in the suppression in resistivity under applied electric field and hence negative ER. At higher applied electric field $> 70$kV/cm, the electron charge density at YCMO layer becomes saturated resulting in almost invariance in ER with applied electric field. Upon application of negative electric field to the junction, opposite phenomenon occurs resulting in the increase in junction resistance thereby positive ER [27] which varies slightly with applied negative electric field. Non-monotonous and fluctuating variation in ER under negative applied electric field can be due to the disorder and inhomogeneity at the interface and manganite layer [9, 26].
4.8 Capacitance – Voltage Characteristics:

Figure 4.8 shows the capacitance – voltage (C – V) characteristics recorded at different temperatures for both the junctions annealed at (a) 700°C and (b) 900°C exhibiting butterfly shaped C – V behavior having a non-linear variation with applied voltage indicating the typical ferroelectric nature of the junctions. Capacitance is found to increase with increase in temperature in both the junctions which is due to the thermal excitation induced movement of charge carriers resulting in the decrease in thickness of interface thereby enhancement in capacitance with temperature, since interface is insulating in nature mainly due to the existence lattice mismatch, structural strain and structural disorder at the interface. Capacitance measured for lower annealed junction is larger than that for higher annealed junction which may be attributed to larger interface strain. It is important to notice the zero shift in C – V plots of lower annealed junction at all the temperatures studied. Generally, trapping of positive (negative) charge carriers results in the zero shift in C – V towards negative (positive) applied voltage. For the present case of 700°C annealed YCMO / Si junction, zero shift is found towards positive applied voltage suggesting the trapping of electrons at the interface resulting in the small current (figure 4.3) and large junction resistance (inset of figure 4.7) in lower annealed junction. Strong correlations between I – V, C – V and transport properties (junction resistance) suggest that interface plays an important role in governing the transport across the junctions.
Figure 4.8: Temperature dependent capacitance–voltage (C–V) characteristics of nanostructured Y$_{0.95}$Ca$_{0.05}$MnO$_3$/Si films annealed at 700°C and 900°C.
Conclusions:

We have successfully grown single phasic polycrystalline \( Y_{0.95}Ca_{0.05}MnO_3 / Si \) (YCMO / Si) films annealed at different temperatures using chemical solution deposition (CSD) method. Temperature dependent \( I - V \) and \( C - V \) characteristics clearly show a strong dependence on film – substrate interface. Variation in \( I - V \) characteristics with temperature and annealing process has been understood on the basis of interface modifications. Various models and theories have been used to understand appropriate mechanism responsible for the transport across the interface and space charge limited conduction (SCLC) has been found to be most appropriate mechanism revealing important role of interface in governing the transport properties of the junctions. Effect of temperature and annealing process on the interface has been reflected in the ratio of free to trapped electron density across the interface. Large rectifying ratio \( \sim 2.2 \times 10^4 \) has been obtained in higher annealed junction. Variation in electroresistance (ER) \( \sim 600\% \) has been discussed on the basis of annealing induced modifications in the film – substrate interface. State of the interface dependent ratio of the free to trapped electron density has been correlated with the \( C - V \) behavior and its zero shift observed in lower annealed junction.
References:


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