Fe-ion implantation in pulse laser deposited La$_{0.75}$Ca$_{0.25}$MnO$_3$ films: Conversion electron Mössbauer spectroscopy and X-ray diffraction studies

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MS received 20 October 1999; revised 14 January 2000

Abstract. Oriented La$_{0.75}$Ca$_{0.25}$MnO$_3$ (LCMO) films have been deposited by pulsed laser deposition (PLD) method on (100) LaAlO$_3$ substrates. Ion-beam technique is used to introduce a very low concentration of $^{57}$Fe in LCMO film. The deposited films were subjected to 100 keV $^{57}$Fe$^+$ implantation with different fluences at room temperature. The main motivation of this work was to study the influence of implantation on the transport mechanism in materials exhibiting colossal magnetoresistance (CMR) property. It is observed that Fe implantation drastically affects the structural and magneto-transport properties. The samples were characterized using the X-ray diffraction (XRD) technique, conversion electron Mössbauer spectroscopy (CEMS) and resistance temperature ($R$–$T$) measurements.

Keywords. Pulsed laser deposition; ion-implantation; colossal magnetoresistance; X-ray diffraction; Mössbauer measurements.

1. Introduction

Colossal magnetoresistance (CMR), a large resistivity change in response to applied external magnetic field, has recently been observed in perovskite oxides of the type R$_{1-x}$A$_x$MnO$_3$ (R = La, Pr, Nd; A = Ca, Sr, Ba) (Chahara et al 1990; von Helmolt et al 1993; Jin et al 1994; Millis et al 1995). The phenomenon has attracted great interest because of its tremendous technological applications in magnetic storage industries (Dong et al 1996; Guo et al 1997). Current research is going on for improvements in both the magnetic sensitivity and temperature dependence of the magnetoresistive response of these oxides.

Despite the exhaustive study on the effects of the rare earth replacement by divalent metal ions in these manganites, very little is known about the influence of the substitution at Mn site, the heart of double-exchange, with other elements. Blasco et al (1997) reported partial substitution of Mn by Al in LCMO, leading to highest CMR ratios at low temperatures. The influence of Fe substitution (Damay 1996) on Sm based compounds and the effect of Al substitution (Martin et al 1996) on Pr based compounds have been reported. Fe doping (Ahn et al 1996) have consistently suppressed conduction and ferromagnetism. The physics governing the observed properties has still not been fully understood and Mn$^{3+}$–O–Mn$^{4+}$ chains are believed to be responsible for the observed transport and magnetotransport behaviour. Any disturbance in these chains should in turn affect the properties. Hence, we were motivated to selectively introduce $^{57}$Fe at the magnetic Mn site by ion-beam technique. Fe was chosen because of its compatible ionic radii and valence chemistry ($d$ shell characteristics), with Mn atom. Also, Fe being a Mössbauer isotope, perturbation at the Mn site could be studied by conversion electron Mössbauer spectroscopy (CEMS).

In the present work, CEMS and XRD studies of $^{57}$Fe ion implantation effect in LCMO films are reported. Using implantation we are able to introduce a dilute and controlled quantity of impurities. It has been observed that implant–anneal (Patil et al 1996) cycle can effectively tailor properties of LCMO system. Thus, the physical properties can be parametrized without many disturbances to the basic LCMO structure provided the defects are suitably annealed. Our main interest is to study the changes produced by nuclear energy loss in the subsurface region (few hundred Å deep) of the film and therefore medium energy ions (100 keV) have been selected.

2. Experimental

Oriented LCMO films, 3000 Å thick, were deposited on (100) LaAlO$_3$ substrates by pulsed laser ablation tech-
nique using a KrF excimer laser (Lambda Physik LPX200, 248 nm, pulse width $t_p = 20$ ns) (Patil et al 1996). The high structural quality of films was confirmed by XRD (Philips PW1729). The resistance versus temperature ($R$–$T$) measurements were carried out using a four-probe method. For magnetoresistance measurements, a maximum field of 1 Tesla was applied. The film plane and current direction were kept parallel to the field direction. The percentage CMR was calculated by the relation

$$\left(\frac{R_H - R_0}{R_0}\right) \times 100\%,$$

where $R_H$ is the resistance with the field applied and $R_0$ the zero field resistance.

Using TRIM94 programme for the simulation of the implantation process (Ziegler et al 1985), the projected range ($R_p$), for 100 keV $^{57}$Fe$^+$ in LCMO is estimated to be 400 Å. The thickness, 3000 Å, was chosen to avoid any substrate induced strain effects and possible film-substrate interdiffusion while annealing the film at elevated temperatures. LCMO films were implanted at room temperature with 100 keV $^{57}$Fe ions at fluences between $1 \times 10^{16}$ ions/cm$^2$ – $3 \times 10^{16}$ ions/cm$^2$. $^{57}$Fe implantation was carried out at the Institut De Physique Nucleaire De Lyon, Universite Claude Bernard, Lyon, France. The fluence rate was maintained at 2 µA/cm$^2$ during implantation. The as-deposited and implanted films were characterized using XRD, resistivity measurements and CEMS. The CEMS measurements were done using a constant acceleration $^{57}$Co : Rh Mössbauer source. The implanted samples were subjected to thermal annealing at 750°C for 3 h in flowing oxygen ambient at 760 Torr.

3. Results and discussion

Figure 1a shows the XRD for the as-deposited LCMO film on (100) LaAlO$_3$ substrates. Observation of only (001) peak in XRD spectrum suggests that LCMO film is c-axis oriented. Figure 2 shows the corresponding $R$–$T$ curve for the as-deposited LCMO film. The peak in $R$–$T$ curve occurs at $T_p = 220$ K. The lower value of $T_p$ as compared with the earlier reports (Patil et al 1996; Lanke 1999) is possibly due to the small oxygen stoichiometry difference in the films. The corresponding CMR data for the as-deposited LCMO film is shown in the same figure. It has a maximum value of CMR at 202 K, 55%, at the peak. The activation energy calculated from Arrhenius plot of ln$[R]$ versus $1/T$ was found to be 77 meV, which matches well with the earlier reported data for such system (Patil et al 1996; Lanke 1999). Thus, our samples are of quality, with property consistent with best reported values in the literature.
Figure 3 shows the normalized resistance ($R_T/R_{300\, K}$) versus temperature for the $^{57}$Fe implanted films at different fluences. It is observed that though the overall resistance behaviour is unchanged, the resistivity of the film increases by a large amount due to the defects formed as a result of implantation. As fluence increases, the rate of change of normalized resistance becomes faster. Interestingly, after implantation, at all the studied fluences, the resistance more or less remains constant below 180 K. Another observation is that, the implanted films do not show CMR effect. This is probably due to the fact that the heavy ion implantation leads to formation of defects and huge pockets of amorphous materials. This is confirmed from XRD (figure 1b depicts a single representative case of a film implanted at $3 \times 10^{16}$ ions/cm$^2$). As can be immediately observed, after Fe implantation LCMO peaks are completely suppressed, note that no other spurious peaks are present. Thus, the films loose their crystalline property and resistance increases drastically.

Figure 4 shows CEM spectra of LCMO films implanted at various fluences. Table 1 summarizes various Mössbauer parameters viz. isomer shift (IS), quadrupole splitting (QS), line width (W) and relative intensity (RI). It is clear from the figure that $^{57}$Fe–LCMO show quadrupole splitting which is quite large. This large splitting is an indication of the fact that implanted $^{57}$Fe ions are sitting in a highly non-cubic site. There is a slight asymmetry in the splitting lines; probably due to distribution of the environment around $^{57}$Fe isotope. With increase in the implanted dose the overall picture of CEMS does not change much. A cursory interpretation would be that the $^{57}$Fe implantation has lead to amorphous LCMO matrix: but the line widths indicate that amorphization may not be uniform. Thus combining the results of XRD and CEMS, we can say that implantation gives rise to small crystallites of $^{57}$Fe–LCMO on a microscopic level, which are polycrystalline pockets; and the overall picture may look to be amorphous.

Annealing is known to improve the properties of CMR films (Patil et al 1996; Lanke 1999). Hence we have subjected the $^{57}$Fe implanted LCMO films to high temperature annealing at 700°C for 3 h. The $R$–$T$ curve in figure 5 shows increase in resistance of LCMO film with...
decrease in temperature. During annealing it may be possible that the \(^{57}\)Fe atoms get sufficient thermal energy to occupy the Mn site. The films could not regain their CMR property even after annealing. From the XRD data for annealed film (figure 1c), it is clear that there is no improvement in the structural quality of the films.

CEM spectra in figure 6 show that after annealing of the film, quadrupole splitting has reduced drastically. This might mean that the microscopic environment around \(^{57}\)Fe is going towards more symmetric site, which indicates that \(^{57}\)Fe goes to the Mn-site because Mn\(^{3+}\) and Fe\(^{3+}\) have identical ion size (Jonker 1954). But if this is the case, we should get CMR effect in the annealed case; however, we do not observe this even after annealing the film. If the film grows into a polycrystalline material, then probably

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**Table 1.** CEMS data for 100 keV \(^{57}\)Fe implantation in LCMO films.

<table>
<thead>
<tr>
<th>Dose (ion/cm(^2))</th>
<th>1.2 \times 10^{16}</th>
<th>2.4 \times 10^{16}</th>
<th>3.0 \times 10^{16}</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>As implanted</td>
<td>Annealed at 700°C</td>
<td>As implanted</td>
</tr>
<tr>
<td>IS (mm/s)</td>
<td>0.24</td>
<td>0.36</td>
<td>0.25</td>
</tr>
<tr>
<td>QS (mm/s)</td>
<td>1.21</td>
<td>0.43</td>
<td>1.14</td>
</tr>
<tr>
<td>W (mm/s)</td>
<td>0.52</td>
<td>0.43</td>
<td>0.55</td>
</tr>
<tr>
<td>RI (%)</td>
<td>97.10</td>
<td>96.00</td>
<td>98.80</td>
</tr>
<tr>
<td>IS (mm/s)</td>
<td>0.02</td>
<td>0.27</td>
<td>0.03</td>
</tr>
<tr>
<td>QS (mm/s)</td>
<td>0.13</td>
<td>0.00</td>
<td>0.09</td>
</tr>
<tr>
<td>W (mm/s)</td>
<td>0.24</td>
<td>0.23</td>
<td>0.24</td>
</tr>
<tr>
<td>RI (%)</td>
<td>0.90</td>
<td>4.00</td>
<td>0.20</td>
</tr>
</tbody>
</table>

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**Figure 5.** \(\ln(R_T/R_{300K})\) versus \(T\) for the \(^{57}\)Fe implantation followed by annealing.

**Figure 6.** CEMS for the \(^{57}\)Fe implantation followed by annealing.
$^{57}$Fe-ion implantation in $\text{La}_{0.75}\text{Ca}_{0.25}\text{MnO}_3$

CMR would be observed at low temperature. We were unable to access such temperatures.

It has been seen previously (Vedawyas et al 1997) that $^{57}$Fe implantation in YBCO leads to excess oxygen intake and $^{57}$Fe acts as gatherer of oxygen in the sample. When one compares $^{57}$Fe implantation in LCMO case, it may be possible that $^{57}$Fe collects excess oxygen leading to highly asymmetric electric field effects which give rise to such large values of quadrupole splitting. It may be mentioned here that the CEM spectra show that $^{57}$Fe is not isolated in the LCMO matrix. Neither are there any indications of Fe$_2$O$_3$ or Fe$_3$O$_4$ complexes. Thus the bonding and electronic structure of $^{57}$Fe could be quite complex.

The results may be interpreted in the following way. The metallic nature after implantation may be due to the presence of implantation-related induced electronic states introduced in the band. Since the fluence value is very high ($10^{16}$ ions/cm$^2$) more scattering events take place leading to overall increase in resistance value (by 4 orders) compared with the as-deposited film. The transport mechanism itself appears different. After annealing the films in the oxygen atmosphere, it may be possible that the Fe is going to Mn site and the system is becoming more cubic.

4. Conclusions

High dose Fe implantation of LCMO thin films, causes a degradation of properties by drastically increasing the resistivity and loss of CMR property. Structurally, the crystalline quality of the starting as-deposited films is also affected. Annealing probably causes Fe to occupy some of the Mn-sites and thereby affects the LaCa(MnFe)O transport picture. This controlled incorporation of dopants by ion-beam method establishes the viability of the implantation technique to impart modification to CMR properties.

Acknowledgements

We would like to acknowledge Prof. G Marest for carrying out $^{57}$Fe implantation and CEMS study. We are thankful to the Head, Physics Department, Pune University, for providing experimental facilities to carry out this work. The help rendered by Dr R Shreekala for fruitful discussions is appreciated.

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