Synthesis and Characterization of Nano-structured Nd-Ca-Mn-O Thin Films

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Abstract: *CMR manganite nanostructured $Nd_{0.7}Ca_{0.3}MnO_3$ (NCMO) thin films have been prepared by the Chemical Solution Deposition method (CSD). CSD is an easy and cost effective technique. Thin films were prepared by spin coating of the precursor solution of concentration, 0.4 M on $LaAlO_3$ (100) substrate, done pyrolysis at 350º C for few minute and kept at three different annealing temperatures. The thin film structure and epitaxy were clearly improved by the 0.4 M concentration of the spin coating solution. All thin films displayed excellent electrical properties such as a low resistivity and very high metal - insulator transition temperatures T_{MI}. Morphological studies were done by AFM & the grains found distributed uniformly in rounded shape.*

Key words: Thin films, XRD, AFM, Magnetoresistance, CMR.

1. INTRODUCTION:

Nano-science and Nano-technology are hottest fields in science, business and news now-a-days. The research advancement in nano-materials and related nano-technology lead to a renewal of interest into the synthesis and characterization of variety of materials for achieving desired properties [1]. In the last years, there has been extensive research activity in the study of the transport and magnetic properties of manganite films and multilayers. The renewed interest in these materials is due to their CMR effect and its possible technological applications [2]. For this reason, fabrication of thin films with the best surface morphology and controlling their magneto-transport properties is essential for making magneto-resistive devices. In order to achieve the desired properties and functions, the synthesis procedure plays an important role. For obtaining bulk polycrystalline mixed oxide compounds, Solid State Reaction (SSR) method is commonly used while thin films are deposited using Chemical Evaporation, Sputtering or Laser Deposition techniques. For obtaining oxide thin films on suitable substrates, Chemical Solution Deposition (CSD) is an easy and cost-effective technique. For obtaining fine or nano sized particles in the bulk form materials, CSD, sol-gel/citrate-gel and co-precipitate techniques are useful [3].

2. MATERIALS :

The precursor solutions of the high purity (99.9 %) Sigma Aldrich chemicals were prepared from neodymium acetate hydrate $Nd(C_2H_3O_2)_3{\cdot}H_2O$, calcium acetate hydrate $C_4H_8CaO_5$ and manganese (II) acetate tetra hydrate $(CH_3COO)_2Mn{\cdot}4H_2O$ and also analytical grade distilled water was used in precursor solution preparation.

3. METHOD :

The solution of NCMO was prepared by mixing the component solutions in the correct proportion to produce films having the composition $Nd_{0.7}Ca_{0.3}MnO_3$. The three thin films were prepared by spin coating method putting the solution on clean $LaAlO_3$ (100) (Crystal GmbH, size: 10 mm × 2.5 mm) single crystal substrates using a rotation speed of 6000 rpm for 25 second. Typically three consecutive coatings were done on each film and each coating followed by pyrolysis at 350º C, for 30 minute before annealing at higher temperature. Annealing was done at 800 ºC, 900 ºC and 1000 ºC for 540 minute in oxygen atmosphere. Each coating produced a film of thickness ~75 nm. Figure 1 illustrates a schematic diagram of $Nd_{0.7}Ca_{0.3}MnO_3$ manganite thin film synthesis.

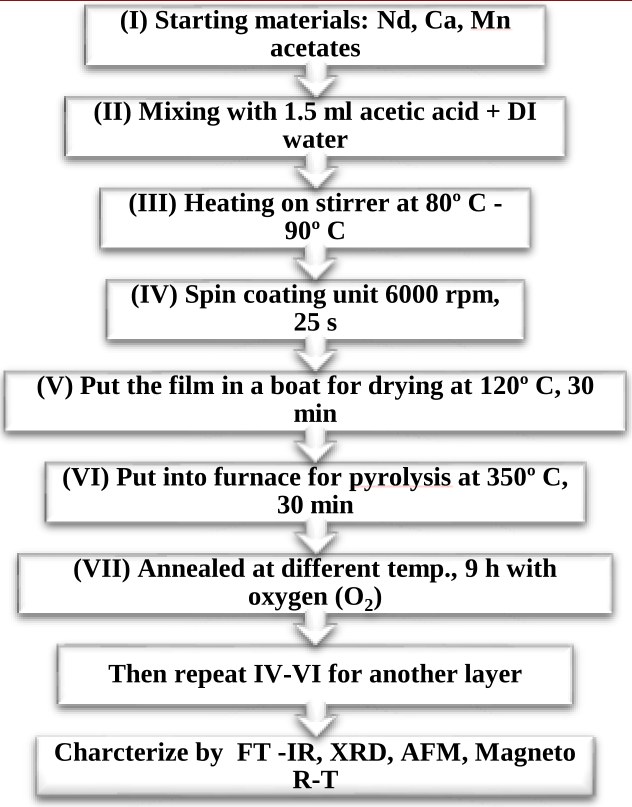

FIGURE 1. Schematic diagram of $Nd_{0.7}Ca_{0.3}MnO_3$ manganite thin film synthesis**.**

4. DISCUSSION:

X-ray diffraction (XRD) was carried out at room temperature using a Siemens D5005 Powder Diffractometer with Cu-kα radiation to check the phase composition and orientation of the film. Fourier Transform Infrared Spectroscopy (FTIR) study was carried out using a Thermo Nicolet spectrometer. The spectra confirm the formation of revealed compound. The surface morphology and thickness were observed by using in tapping mode Atomic Force Microscopy (AFM). DC resistivity measurements were done by the four probe method. Magnetoresistance measurements were carried out up to the field of 8T.

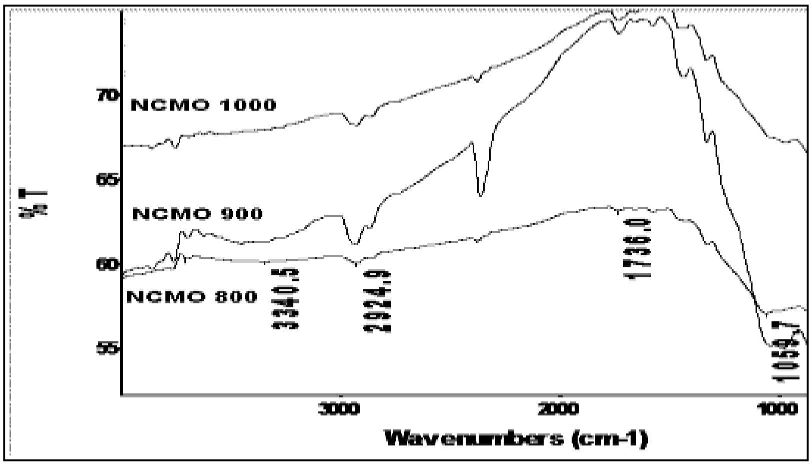

FIGURE 2. FT-IR Spectra of $Nd_{0.7}Ca_{0.3}MnO_3$ thin films annealed at 800 ºC, 900 ºC & 1000 ºC.

Fourier transform spectroscopy (FT-IR) was done for the thin film samples of NCMO prepared at different annealing temperature of 800 ºC, 900 ºC & 1000 ºC for 540 minute. Figure 2 depicts the FT-IR spectroscopy for the thin films of NCMO800, NCMO900 & NCMO1000. The FT-IR spectrum was performed for 400 - 4000 cm^{-1} range. Transmittance FT-IR spectra of these thin films confirmed the development of the perovskite phase. In addition, the spectroscopy study helped to identify intermediate compounds formed in the crystallization process that cannot be detected with X-ray diffraction (XRD). The FTIR spectra of the NCMO thin film annealed at 800 ºC showed very characteristic spectra inorganic nitrates absorption bands at ~ 1736 cm^{-1}, 1300 cm^{-1}, & 830 cm^{-1}. There also may be the typical water bands ~ 3400 cm^{-1}, & 1640 cm^{-1}. No difference in the spectra except peak intensities was detected for

NCMO thin film annealed at 900 ºC. For film annealed at 1000 ºC, all the absorption bands vanished from the film material and showed clear spectra [3].

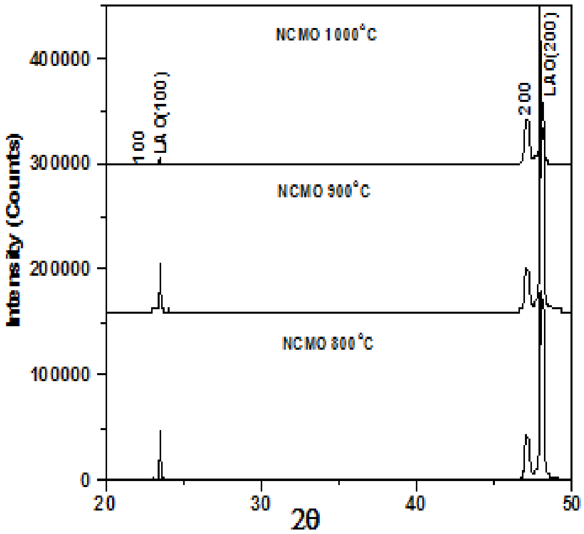

FIGURE 3. XRD patterns of $Nd_{0.7}Ca_{0.3}MnO_3$ films, annealed at 800º C, 900º C & 1000º C.

The structure of each $Nd_{0.7}Ca_{0.3}MnO_3$ film was determined by X-ray diffraction (XRD) using a Siemens D5005 X-ray diffractometer with the CuKα radiation with 0.02° step time at room temperature. The X-ray diffraction patterns of NCMO films coated on $LaAlO_3$ (l00) substrates annealed at 800 ºC, 900 ºC, & 1000 ºC for 540 minute. XRD measurements revealed that the films were grown highly a-axis oriented [4].The films were also found with no peaks corresponding to secondary phases or organic contaminants in these diffraction patterns. These results also indicate that NCMO films on LAO (100) are grown in (100), (200) direction normal to the substrates. In order to study the effect of the substrate on the structure of the deposited films, the (200) peaks in the XRD patterns were analysed. The $LaAlO_3$ (100) substrate is nearly cubic with a lattice constant a = 3.79 Å. Bulk NCMO is orthorhombic with $a/\sqrt{2} = 3.879$, $b/\sqrt{2} = 3.866$ and $c/2 = 3.856$. The a-axis lattice constant of the NCMO films annealed at 800, 900 and 1000 °C on LAO are 3.834 Å, 3.824 Å & 3.815 Å respectively. These are slightly different from the lattice parameter of LAO which have cubic symmetry. As the annealing temperature increases, the lattice parameter of NCMO decreases.

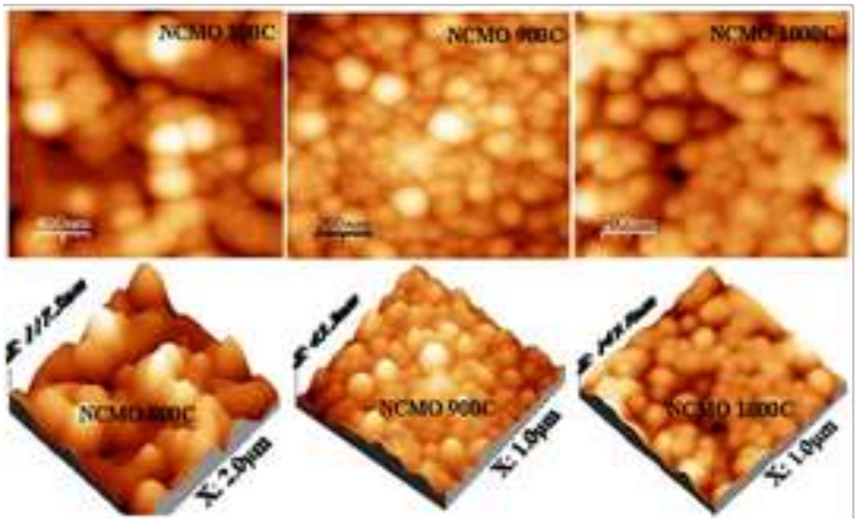

FIGURE 4. AFM images of $Nd_{0.7}Ca_{0.3}MnO_3$ annealed at 800º C, 900º C & 1000º C [Top view & 3D view].

In order to get information about the morphology, coating effectiveness, grain size, and surface roughness of the films of $Nd_{0.7}Ca_{0.3}MnO_3$ (NCMO) grown on LAO (100) substrate were examined using an atomic force microscope (AFM) in contact mode at room temperature. For CMR films, single crystalline $LaAlO_3$ is usually used as substrate, which is advantageous for the growth of epitaxial films. The parameter such as average height, root mean square roughness (area r.m.s.), maximum range (Zm) were determined by AFM. In contact mode, the AFM images are produced by dragging a vibrating cantilever with Si_3N_4 tip across the surface. High resolution two dimensional topographic AFM micrographs and inserted image of mesh average corresponding to $Nd_{0.7}Ca_{0.3}MnO_3$ films annealed at 800 ºC, 900 ºC, and 1000 ºC, for 540 minute are shown in Figure 4. The films images confirmed that the films consist of nano-scaled granular crystallites with a narrow distribution of grain size and quantities of grain boundaries. The grains become very clear with sharper grain boundaries with increasing annealing temperature. In the NCMO800 the presence of 2D some holes and big grain on the terraces signal an incomplete layer coalescences. There are some 2D islands that have nucleated at the steps, on the upper terrace part. On the other hand, in NCMO900, there are less holes and islands. The surface roughness values are 36 nm, 33 nm, 18 nm for the thin films annealed at 800º C, 900º C & 1000º C respectively.

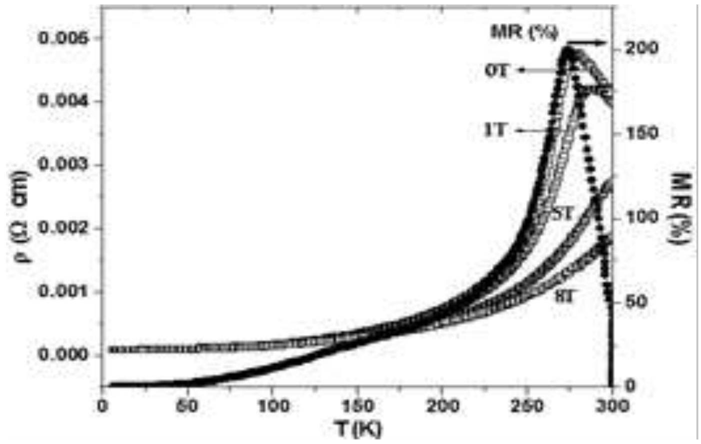

FIGURE 5. Temperature dependent Resistivity & MR of 800º C annealed $Nd_{0.7}Ca_{0.3}MnO_3$ film.

The electrical transport constitutes probably the most attractive physical property of the manganites. Electrical resistivity of CMR manganite film was obtained by the four point technique with temperature controlled holder. Resistivity values have been calculated using the measured resistance and knowing the corresponding values of the cross section (A) and length (l). Films are rectangular shaped, and assumed that parallel current lines develop along the long dimension (l), and taking the suitable expression [5]:

$$\rho = \frac{RA}{l}$$

The electrical resistivity of an $Nd_{0.7}Ca_{0.3}MnO_3$ thin film annealed at 800 ºC as a function of temperature under different magnetic fields are shown in figure 5. Recorded resistance measurements were taken from 4.5 K to 300 K. The mentioned annealed temperature film demonstrates abrupt resistivity maximum in experimental curves provides information about the transition from metal to insulator (T_{MI}). Looking at the ρ vs. T curves with the applied magnetic field of 0 T, 1T & 5T, for NCMO annealed at 800 ºC, it is possible to note the presence of a transition from a metallic (M) - insulator (I) transport for the films. One can see that the T_p increases with increasing magnetic field, where the T_{MI} values are 248 K, 295 K and ~ 298 K for the applied magnetic field of 0 T, 1T & 5T respectively. Moreover, ρ(T) results show that the measured metal – insulator transition temperature (T_{MI}) behaviour, under the magnetic field at 0 T, 1 T & 5 T are 248 K, 287 K & 290 K respectively and the corresponding resistivity (ρ) values are 0.0047, 0.0042, & 0.0017 Ω cm respectively[6].

5. CONCLUSION:

In summary, $Nd_{0.7}Ca_{0.3}MnO_3$ epitaxial thin films have been successfully fabricated on $LaAlO_3$ (LAO) single crystal substrate by using chemical solution deposition (CSD) method. Samples with identical cation stoichiometry $Nd_{0.7}Ca_{0.3}MnO_3$ showed a strong dependence of electrical properties on the substrate material used for thin film deposition. Chemical solution deposition (CSD) technique is playing a significant role in preparing high quality films. This method has the advantage of quick prototyping so that a large number of film compositions can be quickly tested in a cost-effective manner. Given the fact that in modern IC processing, Cu interconnects are grown using chemical deposition methods, these methods are compatible with large size wafer processing routes. NCMO films have been observed to exhibit a cubic lattice with around a = 3.83 Å, nano-crystalline morphology and significant magneto-resistance ratio over a wide range of temperature. The structural data confirmed that a film grown onto LAO (100) is under the compressive strain. In the cases, annealing temperature increase leads to a partial removal of the strain induced. The surface morphology results also confirmed that the NCMO films show clear grain morphology and orientation with grains in nanometer range and the grains become more evidently with sharper grain boundaries with increasing annealing temperature. The ρ – T curves of thin film clearly shows metal – insulator (T_{MI}) transition behaviour.

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