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Growth and study of $PrCoO_3$ thin films nanostructures deposited on various substrates

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ABSTRACT

Thin film nanostructures of $PrCoO_3$ were deposited on (111) Si, (001) $LaAlO_3$ (LAO) and (001) SrTiO3 (STO) substrates by pulsed laser deposition technique (KrF excimer laser, wavelength =248 nm). These films were characterized by x-ray diffraction (XRD), scanning electron microscopy (SEM), x-ray photoelectron spectroscopy (XPS) and Raman Spectroscopy techniques. XRD results reveal that all films are single phase and films on silicon substrates are polycrystalline while films deposited on LAO and STO are highly oriented along c-axis. XPS results clearly indicate that our films are free from impurity and chemical state are as expected for $PrCoO_3$.

Keywords: Pulsed laser deposition, XRD,XPS

Introduction

The peroveskite type transition metal oxides materials have been gained much interest in the research activities due emergence of exotic properties such as charge ordering, orbital ordering, phase separation, colossal magneto resistance etc.**1** Cobaltates $ACoO_3$, where A is the rare earth element, form an interesting class of compounds in the perovskite family. These compounds show insulator to metal transition with increase in temperature.**2** It is believed that such transition occurs due to the thermally driven spin state transition of Co^{3+} ions.**3** A spin state transition was also proposed for $PrCoO_3$, for which the -(*T*) curve exhibits a broad minimum around 200 K.**4** Fierro et al.**5** had reported the reduction study of $PrCoO_3$ using X-ray photo electron spectroscopy and detect two type of oxygen one at lattice oxygen (binding energy = 528.4 eV) while other was adsorbed oxygen (at binding energy = 530.9eV). They suggest that the peak at 530.9 eV is associated with reduction of perovskite and subsequent formation of praseodymium hydroxide in the presence of the water molecule generated in the reduction process.

Yoshii et al.6 studied magnetic behavior and showed that $PrCoO_3$ exhibited no magnetic ordering down to 4.5 K. There are various reports on bulk $PrCoO_3$ properties but no reports are available on thin films of $PrCoO_3$ while various reports are available on thin films of $LaCoO_3$ compound.7-9 The thin films of any material has unusual properties compared with corresponding bulk compound because of its growth condition, deposition induced strain, method of deposition etc. To study the exotic physical properties of $PrCoO_3$ thin films, we have decided to grow the thin films of $PrCoO_3$ on various substrates one on Si because Si is lattice mismatch substrate with $PrCoO_3$ and very important semiconducting substrate used in various device applications. LAO and STO are closely lattice match substrates with $PrCoO_3$. There are various thin film deposition techniques but pulsed laser deposition (PLD) is known to best technique for deposition of oxide compounds, Therefore in present study, we have used PLD as thin film deposition techniques. In present paper, to study the effect of substrates on $PrCoO_3$ thin film, we have deposited the films of $PrCoO_3$ on Si, $LaAlO_3$ $SrTiO_3$ substrates using PLD technique and characterize them using different characterization techniques.

Experimental

Thin films of $PrCoO_3$ were deposited on (111) Si, (001) $LaAlO_3$ (LAO) and (001) SrTiO3 (STO) substrates using pulsed laser deposition (PLD) technique (KrF excimer laser,

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wavelength = 248 nm). The substrate temperature during deposition was kept at 680 °C and depositions were done at O_2 partial pressure of 300 mTorr. Bulk $PrCoO_3$ powder used for target preparation was prepared by combustion method. This pallet for PLD target was obtained by sintering the pallet at 1200 °C for 12 hours. The crystal structure and single phase of bulk target was confirmed by x-ray diffraction measurement. The substrate to target distance was kept 4 cm and substrate heating was done using a heater which temperature was controlled with DC power supply. The laser energy density at the target was fixed to 2J/cm^2 and pulse repetition rate was 10 hertz. The deposition was done for 20 minutes duration. The thicknesses of the deposited films were ~200 nm as measured by stylus profilometer (Ambios Inc. USA). The crystal structure and phase of deposited thin films were characterized by X-ray diffraction measurement. The X-ray diffraction (XRD) of the films was carried out using Rigaku diffractometer with CuK radiation (=1.54 Å). The surface morphology was examined by scanning electron microscope (SEM) (Joel model: JSM-5600) operating at 20 KV. X-ray photoelectron spectroscopy was employed to get the chemical composition of the thin films. The X-ray photoelectron spectroscopy (XPS) measurements was performed using Omicron energy analyzer (EA 125) instrument with Al K (1486.6 eV) x-ray source. The pressure of the analyzer chamber was in order of 10^{-10} Torr during the XPS measurement. The analysis of different oxidation states of ions was performed by deconvolution of unresolved peaks. The values corresponding to C 1s peak were used as a reference for spectrum analysis. The survey scan spectra for all samples were recorded at 50 eV pass energy while in case of narrow scans the pass energy was kept at 40 eV. For study of the vibrational properties of these films, laser Raman spectroscopy was employed. Raman spectra were recorded at room temperature using Micro Raman spectrometer (Model HR-800, Jobin Yvon) employing He-Ne laser (=632.8nm). The measured resolution of spectrometer is 1 cm^{-1}. Spectra were collected in backscattering geometry using charge-coupled device (CCD) with laser power 9 mW and incident laser power focused in a diameter 2μm. Notch filter is used to suppress the Reighley light.

Results and discussion

Figure 1 shows XRD patterns of $PrCoO_3$ thin films deposited on Si (111), (001) $LaAlO_3$ (LAO) and (001) SrTiO3 (STO) substrates along with respective substrates respectively. XRD patterns are shown in Log scale so that any impurity peak can be identified. We have also plotted corresponding substrate XRD pattern to omit the corresponding substrate XRD peaks from the XRD pattern of the films. The XRD patterns reveal that $PrCoO_3$ films deposited on all the substrates are crystalline and single phase. We do not observed any impurity phase other than the substrate peaks. $PrCoO_3$ films on Si substrates are polycrystalline in nature while films deposited on LAO and STO are oriented to substrate orientation i.e. along (001) plane. From XRD pattern we calculated lattice parameter and particle size of the films. The film peaks were marked by F. The film deposited on Si substrate has (110), (200) and (220) reflections. In this case the intensity of (110) peak is maximum. While the films deposited on LAO and STO substrates are c- axis textured and have (100), (200) and (300) reflections. All the observed XRD peaks of $PrCoO_3$ films can be indexed with cubic phase JCPDS No75-0280.

From the fitting of highest intensity peak of each films, we obtain peak positions and full width and half maximum (FWHM) for each case. These peak position and FWHM values were used to calculate the lattice parameter and particles size of the films. The lattice parameter estimated from XRD pattern for films deposited on Si, LAO and STO substrates are 3.773, 3.788 and 3.783 Å, respectively. These values of lattice parameters are very close to bulk $PrCoO_3$ lattice parameter (3.780 Å). We calculated the grain size (D) of the film using the Debye–Scherrer formula[10] given by D = 0.94 × /(B cos) Where is the wavelength of the x-ray source and B^2= ^{2}-b^2 in which is the full width at half maximum (FWHM) of an individual peak at 2 (where is the Bragg angle) and b is instrumental broadening.

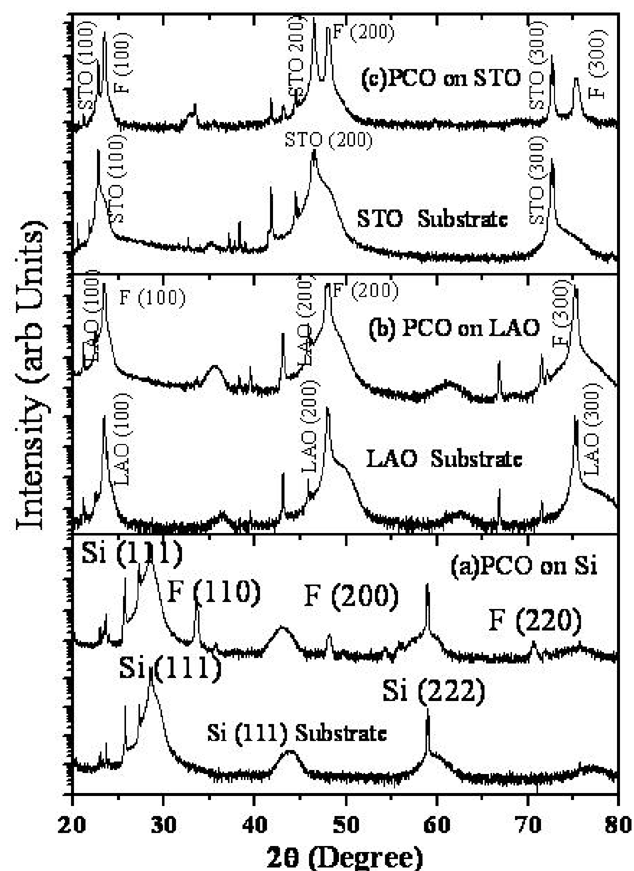


Figure 1: X-ray diffraction pattern of $PrCoO_3$ films deposited on Si (111), LAO (001) and STO (001) substrates along with corresponding substrate diffraction pattern

The calculated particle size for $PrCoO_3$film deposited on Si substrate is 37 nm and film deposited on LAO substrate is 38 nm while film deposited on STO substrate is 32 nm. From XRD date it is clear that film deposited on LAO have better crystalline quality than other substrates.

After structural characterization we checked the surface morphologies of deposited film by scanning electron microscope (SEM). Figure 2 shows the SEM micrographs taken for $PrCoO_3$ films deposited on different substrates. It is clear from SEM images that the surfaces of all films are smooth and have less particulate in the films. It is also clear

from SEM micrographs that surface morphologies of the deposited films are different for different substrates. These observations indicate that substrates affect the surface morphology of the films.

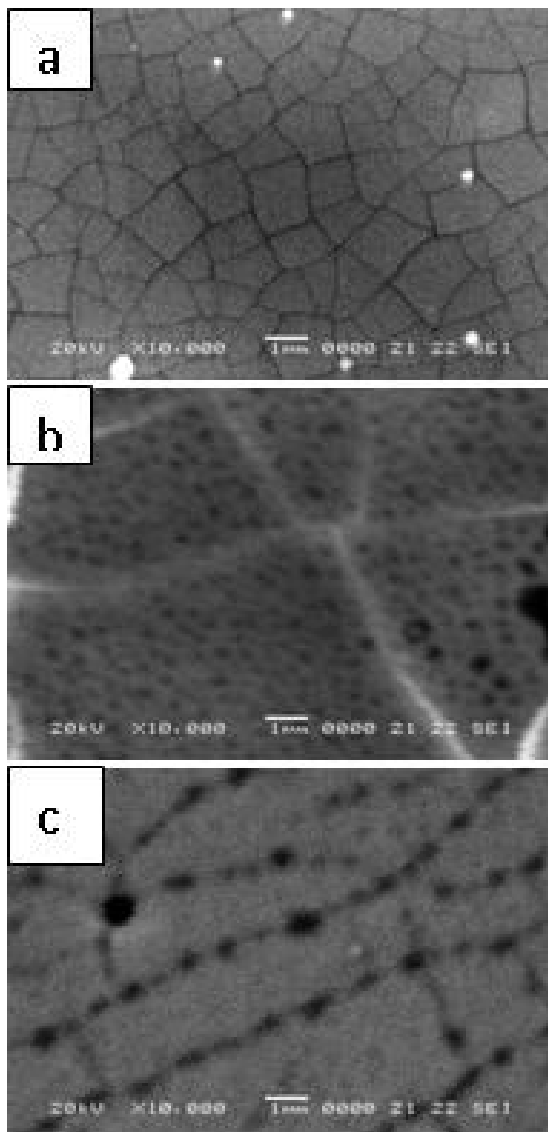
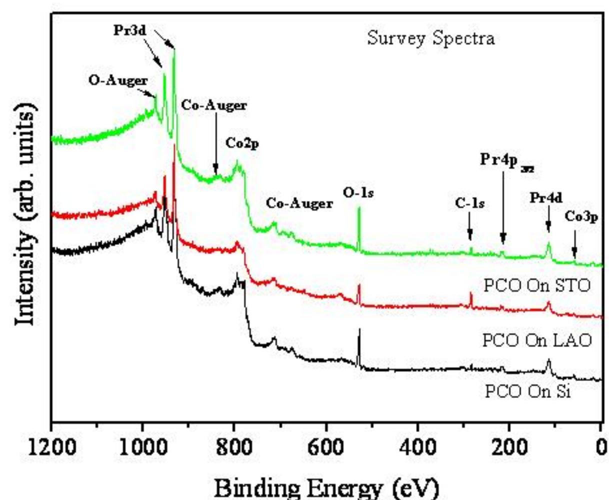


Figure 2: SEM images of the PrCoO3 films deposited on (a) Si (b) STO and (c) LAO substrates

Along with SEM micrographs we have also recorded energy dispersive analysis of x-rays (EDAX) spectra to get the composition of the film. From EDAX analysis we found that the film composition is very close to $PrCoO_3$.

To get the electronic state of different elements (Pr, Co and O) present in the films, we have performed X-ray photoelectron spectroscopy (XPS) measurements on these films. We have recorded survey scan spectra of these films to get information about various elements present in the surface of the films. From the XPS survey spectra as shown in figure 3, we have identified that only Pr, Co and O are present with very small contribution of C which was expected because films surfaces were exposed to air before XPS measurements and also the films are deposited at high vacuum. The positions of various photoemission peaks are marked in the spectra for



elements present in the samples.

Figure 3: Survey scans of X-ray photoemission spectra for $PrCoO_3$ thin films deposited on Si (111), LAO (001) and STO (001) substrates

To further get the charge states of Pr, Co and O ions, we have performed detailed scans for Pr-3d, Co-2p and O-1s core level spectra (not shown here).

Table 1: Experimental binding energies (eV) for XPS core level main peak of $PrCoO_3$ thin films deposited on Si, LAO and STO substrates

Cove level	$PrCoO_3$/Si	$PrCoO_3$/LAO	$PrCoO_3$/STO
$Pr3d_{5/2}$	932.6 928.1	932.7 928.3	936.6 928.1
$Co2p_{3/2}$ $Co2p_{1/2}$	779.3 794.5	779.7 794.9	779.6 794.8
O1s	528.7	528.7	528.6

The core level spectra fitted to get peak position and FWHM which was used get the charge state of various elements. Table 1 list all the peak positions of various core levels spectra present in the samples.

Figure 4 shows Raman spectra of $PrCoO_3$ films deposited on Si, LAO and STO substrates. The Raman modes for film deposited on Si substrate are observed at 149, 458, 505, 571 and 657 cm^{-1}. While Raman modes for film deposited on STO substrates are observed at 148, 455, 502, 558 and 650 cm^{-1}. Raman modes for film deposited on LAO substrates are observed at 148, 455, 503, 563 and 653 cm^{-1}. For bulk $PrCoO_3$ samples, the positions of three main Raman active modes E_g, F_{2g} and A_{1g} are reported[11] at 690, 480 and 200 cm^{-1}, respectively. The two of the five observed Raman modes values are close to the reported Raman modes of bulk $PrCoO_3$, namely F_{2g} and A_{1g} Raman active modes. The observation of

five modes in thin films may be due to presence of deposition induced strain in the films.

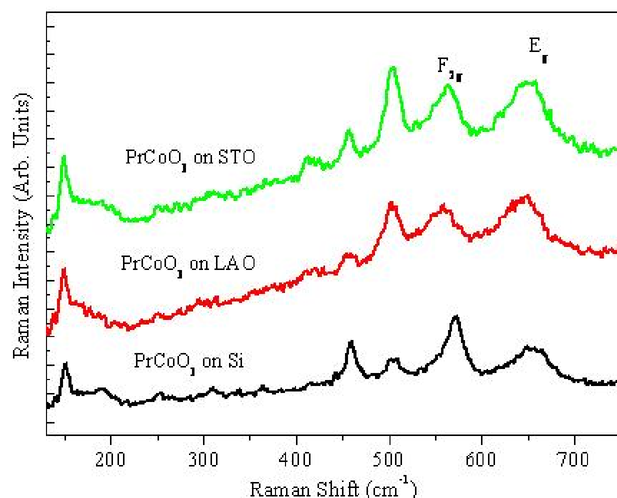


Figure 4: Raman spectra of $PrCoO_3$ thin films deposited on Si (111), LAO (001) and STO (001) substrates

To the best of our knowledge, there are only one report is available in the literature of bulk $PrCoO_3$ Raman spectra while no reports are found for the thin films of $PrCoO_3$. Since all other measurements are confirming to $PrCoO_3$ phase of the films, therefore these Raman modes should be purely related to $PrCoO_3$ thin films.

Conclusion

In conclusion, we have successfully deposited $PrCoO_3$ thin films on Si, LAO and STO substrates by pulsed laser deposition technique. Deposited films are single phase and polycrystalline in Si substrate while c-axis textured in LAO and STO substrates. The surface morphologies of these films indicate that these films are free from particulates and impurity and have different surface morphology for different substrates. XPS spectra reveal that these films have $PrCoO_3$ phase with Pr and Co sates are +3 states these results are similar to bulk spectra. Raman spectra of these films deposited on different substrates are qualitative similar.

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