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Raman spectroscopic studies on pulsed laser deposited nanostructured $LiCoO_2$ thin film cathodes

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ABSTRACT

Thin films of $LiCoO_2$ were prepared by pulsed laser deposition technique. Two important deposition parameters such as substrate temperature and oxygen partial pressure during the thin film deposition were controlled. The Raman data consist of a series of broad bands located between 400 and $700cm^{-1}$ for $LiCoO_2$ films. The Raman band located at $592cm^{-1}$ can be viewed as the symmetric Co-O stretching vibration of CoO_6 groups. This band is assigned to the A_{1g} symmetry. The RS peak position at $484cm^{-1}$ derives from the E_g species. The symmetric motions involve Co-O stretching and O-Co-O bending vibrations. The intensity ratio increased with the increase of substrate temperature. The film deposited at 700°C in pO_2=100 mTorr, indicating that the film had no preferred orientation.

KEYWORDS

$LiCoO_2$ thin films;
PLD, Raman.

INTRODUCTION

Lithiated transition metal oxides such as $LiMO_2$ (Where M=Co, Ni, Mn etc.) have received considerable attention in recent years as high voltage positive electrode materials for use in secondary lithium batteries[1]. Among these, the high cycling stability and high cell potential against lithium makes $LiCoO_2$ an attractive cathode material in the fabrication of all solid state rechargeable microbatteries[2,3]. Its theoretical specific capacity and energy densities are 274mAh/g and 1070Wh/kg respectively.

The layered $LiCoO_2$ consists of a close packed network of oxygen ions with Li and Co ions on alternative (111) planes of the cubic rocksalt sub-lattice. The edges of CoO_6 octahedral were shared to form CoO_2 sheets and lithium ions can move in two-dimensional directions between CoO_2 sheets. Thus the layered $LiCoO_2$ has an anisotropic structure and thereby electrochemical lithium insertion/extraction behaviour must depend strongly on the orientation of the microcrystallites. The growth of $LiCoO_2$ thin films with preferred orientation is known to be crucial. Several thin film deposition techniques such as RF sputtering[2,4], pulsed laser deposition[4-8], electrostatic spray deposition[9] and chemical vapour deposition[10] were employed for the growth of $LiCoO_2$ thin films. A brief literature survey reveals that it is difficult to grow stoichometric and stable c-axis oriented $LiCoO_2$ thin films by several physical vapour deposition methods due to many growth kinetic processes which occur in vacuum or at low oxygen partial pressures.

Pulsed laser deposition (PLD) has been widely recognized as a very promising, versatile and efficient method for the deposition of metal oxide thin films[11]. When PLD is carried out in the atmosphere of a chemically reactive gas (a process known as reactive pulsed laser deposition (RPLD)), the flux of the laser ablated material interacts with the gas molecules all along the transit from the target to the collector surface. The resulting deposited layer was found to have a chemical composition substantially the same as the base or starting material. Preliminary investigations on pulsed laser deposited $LiCoO_2$ thin films were carried out by Julien et al.[5]. Iriyama et al.[6] and studied the electrochemical performance. They observed that the reactivity in single-phase region at potentials more positive than 4.0V was lower than that of randomly oriented films. Poly-crystalline layered $R\bar{3}m$ phase thin films of $LiCoO_2$ were grown by PLD using Nd:YAG laser by Julien et al.[12]. This $LiCoO_2$ cathode active films were found to deliver a specific capacity of $195 mC/cm^2 \mu m$ in the voltage range 2.0-4.2V. In the present study the influence of deposition parameters on the Raman studies of pulsed laser deposited $LiCoO_2$ thin films were reported.

EXPERIMENTAL

$LiCoO_2$ films were grown by pulsed laser deposition technique on silicon substrates maintained at temperatures in the range 200-700°C. $LiCoO_2$ target was prepared by sintering a mixture of high purity $LiCoO_2$ and Li_2O powders (Cerac products) with excess of Li i.e. Li/Co>1.0 by adding Li_2O. The mixture was crushed and pressed at 5 $tonns.cm^{-2}$ to make tablets of 3 mm thick and 13 mm diameter. To get quite robust targets, the tablets were sintered in air at 800°C. The typical substrates i.e. Si wafers were cleaned using HF solution. The target was rotated at 10 rotations per minute with an electric motor to avoid depletion of material at any given spot. The laser used in these experiments is the 248nm line of a KrF excimer laser (Luminics PM 882) with 10 ns pulse with a repetition rate of 10 Hz. The rectangular spot size of the laser pulse was 1×3mm and the energy 300mJ. The target substrate distance was 4cm. The deposition temperature was maintained with thermocouple and temperature controller. During the deposition pure oxygen was introduced into the deposition chamber and desired pressure was maintained with a flow controller.

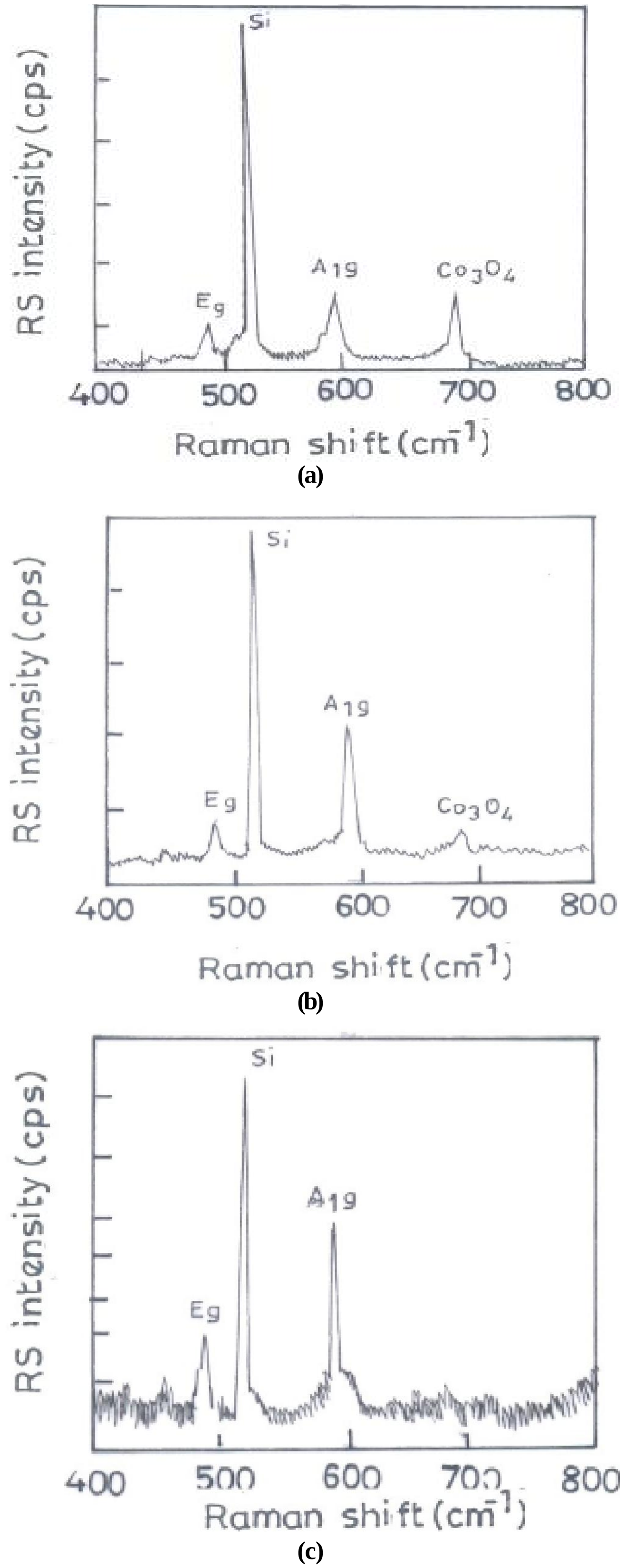
The Raman spectra of $LiCoO_2$ films were recorded between 200 and $1000 cm^{-1}$ at room temperature in a quasi-backscattering configuration at a spectral resolution of $2 cm^{-1}$. The Raman-laser apparatus (Jobin-Yvon U1000) was equipped of holographic grating double-monochromator, an intermediate spatial filter and a computer-controlled photon-counting system. The emission from a laser (Spectra-Physics, 2020 argon-ion) with a wavelength of 514.5nm was used. The frequency stability and the accuracy of the apparatus were checked recording the Raman spectrum of silicon. To avoid sample photo-decomposition or denaturation, RS spectra were recorded using a low power density of $100 W/cm^2$.

RESULTS AND DISCUSSION

Pulsed laser deposited $LiCoO_2$ films are pin-hole free as revealed from optical microscopy and well adherent to the substrate surface. The thickness of $LiCoO_2$ films is 250 nm. The influence of oxygen partial pressure (pO_2) and deposition temperature (Ts) on the Raman studies of the films are systematically studied. The chemical compositional studies made on $LiCoO_2$ films revealed that a minimum of 100 mTorr oxygen partial pressure is required to grow nearly stoichiometric films.

$LiCoO_2$ possesses the R3m space group, D^5_{3d} spectroscopic symmetry. According to the results of the theoretical factor-group analysis, two modes are active in the Raman spectrum (A_{1g} & E_g) of the $LiCoO_2$ crystal[13]. Figure 1(a-c) shows the unpolalized Raman scattering spectra of $LiCoO_2$ films deposited on silicon maintained at 300C in oxygen partial pressure pO_2=100 mTorr as a function of the target composition.

These spectra displayed the Raman active mode of the silicon wafer at $520 cm^{-1}$. The experimental Raman data consist of a series of broad bands located between 400 and $700 cm^{-1}$. The RS peak positions at 484 and $592 cm^{-1}$ of PLD $LiCoO_2$ films are in good agreement with those reported for the $LiCoO_2$ crystal[14]. The vibrational signature of the $LiCoO_2$ matches well the two allowed Raman modes. The peak



(a)

(b)

(c)

Figure 1 : Raman spectra of $LiCoO_2$ thin films deposited from composite target with different concentrations of Li_2O; (a) without Li_2O (b) 10 wt.%, and (c) 15 wt.%

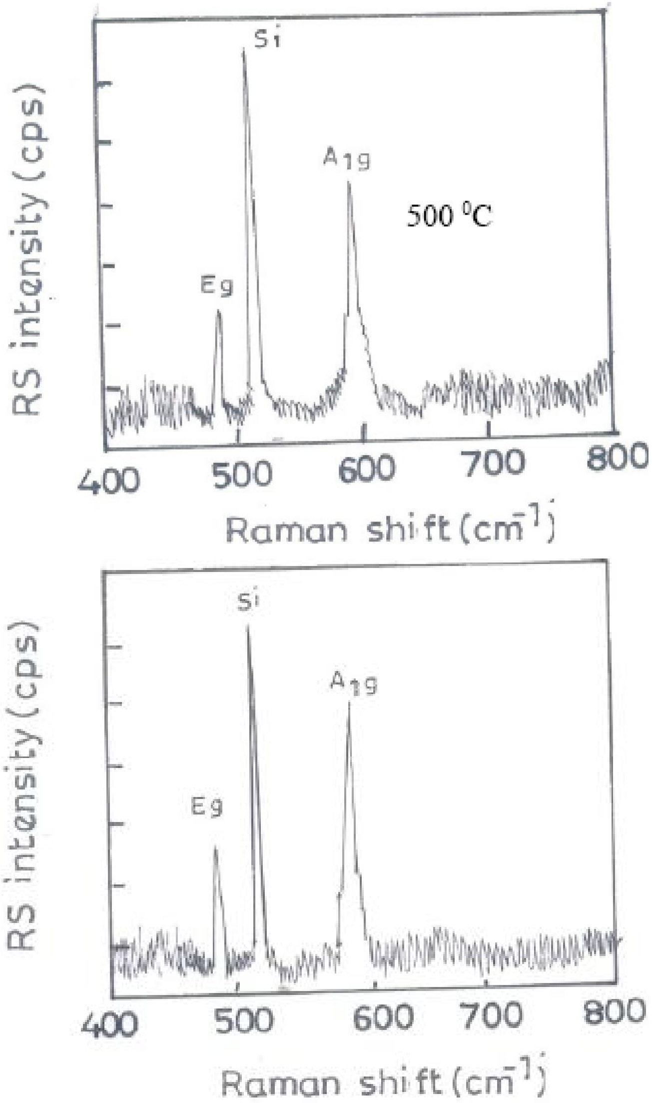


Figure 2 : Raman spectra of $LiCoO_2$ thin films deposited at different substrate temperatures in pO_2=100 mTorr

located at 693 cm^{-1} in Raman spectra (Figure 1(a) and (b)) indicates the presence of Co_3O_4 impurities in the film[15]. The formation of Co_3O_4 is related to lithium loss during the deposition process. In order to compensate this loss we have prepared films from lithium rich targets including addition of 10 and 15% of Li_2O concentration. The corresponding spectra are shown in Figure 1(b-c). Upon addition of Li_2O, the peak at 693cm^{-1} decreased substantially indicating the disappearance of Co_3O_4 species as it is shown in the RS spectra (Figure1(c)). The optimum concentration of Li_2O to compensate the lithium loss must be 15% of Li_2O. $LiCoO_2$ possess the prototype symmetry R-3m of the rock-salt structure, where the cobalt cations reside on the octahedral 3a sites, the lithium ions occupy the octahedral 3b interstices, and the oxygen anions are in a cubic close-packing, occupying the 6c sites[15]. It is also convenient to analyze the RS spectrum in terms of localized vibrations, considering the rock-salt structure built of CoO_6 and LiO_6 octahedra[14]. The Raman band located at $592cm^{-1}$ can be viewed as the symmetric Co-O stretching vibration of CoO_6 groups. This band is assigned to the A_{1g} symmetry in the D^5_{3d} spectroscopic space group. Its broadening could be related with the cation-anion bond lengths and polyhedral distortion occurring in $LiCoO_2$. The RS peak at $484cm^{-1}$ derives from the E_g species. The Raman bands are likely lie to the motions involving mainly the Co-O stretching and O-Co-O bending, as the contributions of the Raman modes are only from the motion of the oxygen atoms.

The polarized scattering spectra show uniaxially (003) textured $LiCoO_2$ thin films. Based on the intensity ratio of Raman spectra, the peaks situated at 484 and $592cm^{-1}$ correspond to the E_g and A_{1g} optical modes of $LiCoO_2$, respectively[14]. The polarization dependence of the recorded spectra is consistent with the prediction for phonon symmetries. These results show that, as expected, the A_{1g} stretching mode should be at higher energy than the E_g bending mode.

Information for the structural quality of the PLD $LiCoO_2$ films can be given considering the Raman data using the shape and the frequency of two peaks located in the low and high frequency region of the spectra. When the PLD films were grown from target with $Li_2O \leq 15\%$, the oscillator strength of the A_{1g} stretching mode of RS spectra rose with a narrow full width at half maximum (FWHM). This phenomenon is due to the well-defined rock-salt structure of the films and the regular distortion of CoO_6 octahedra. As the stretching mode is sensitive to the film morphology, low FWHM values provide evidence for the rock-salt-like structure for samples grown at a high substrate temperature. These spectroscopic results indicate that the conjunction of target composition (lithium-rich), substrate temperature (T_s>300°C), and oxygen partial pressure ($pO_{2=}$100 mTorr) promotes reconstruction of the stoichiometric $LiCoO_2$ layered framework.

Raman spectroscopy is also useful to distinguish between different symmetries in a given material. Figure 2 shows non-polarized Raman spectra of thin films deposited at different temperatures in $pO_{2=}$100 mTorr. The spectra are nonpolarized by the intensity of the A_{1g} peak at $592cm^{-1}$. I_{484} and I_{594} are referred as intensities of the E_g and A_{1g} bands respectively. The I_{484}/I_{594} increased with a decrease in the degree of the c-axis orientation of the films. The film deposited at 700°C in $pO_{2=}$100 mTorr, indicating that the film had no preferred orientation. These results are in good agreement with the results reported by Iriyama et al.[9].

CONCLUSIONS

Thin films of $LiCoO_2$ were prepared by pulsed laser deposition. PLD films were found to be uniform with regard to the surface topography, thicknesses and well adherent to the substrate surface. The Raman band located at $592cm^{-1}$ can be viewed as the symmetric Co-O stretching vibration of CoO_6 groups. The RS peak position at $484cm^{-1}$ derives from the E_g species. The symmetric motions involve Co-O stretching and O-Co-O bending vibrations. The intensity ratio increased with the increase of substrate temperature. The film deposited at 700°C in $pO_{2=}$100 mTorr, indicating that the film had no preferred orientation. These results suggest that the open and porous structured $LiCoO_2$ PLD films find potential applications as binder free electrode in the fabrication of all solid state microbatteries.

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