Synthesis and characterization of $LiCoO_2$ thin film cathodes grown by pulsed laser deposition

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$LiCoO_2$ thin films were prepared by pulsed laser deposition technique. FTIR, Raman and Electrochemical measurements were made on to these films with respect to their deposition parameters i.e. substrate temperature (T_s), oxygen partial pressure (pO_2) in the deposition chamber. The FTIR spectrum displayed the characteristic IR dominant bands at 250 and 554 cm^{-1} for $LiCoO_2$ thin films deposited in pO_2 = 200 mTorr. The Raman data consist of a series of broad bands located between 400 and 700 cm^{-1} for $LiCoO_2$ films. The Raman band located at 592 cm^{-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 484 cm^{-1} derives from the E_g species. Electrochemical titration was made by charging and discharging the cells in the potential range between 2.0 and 4.2 V. Electrochemical potential spectroscopy (ECPS) was performed using 5 mV potential steps. Specific capacity 185 mC/cm^{2}μm was measured for the film deposited in pO_2 = 200 mTorr.

1. Introduction

Solid state microbatteries now in development may help facilitate three-dimensional high-density integrated circuit technology by providing power to components locally rather than from a remote source, thus reducing "crosstalk" between circuits. An integrable microbattery compatible with the dimensions of microdevices will act as a source of power for many single components in integrated circuits and devices. Fabrication of the materials as thin film cathodes for application in all solid state microbatteries has been interesting field of research owing to the miniaturization and the reduced power consumption of many kinds of electronic devices. There is a growing interest in thin film batteries with smaller dimension. The cathode is one of the critical components of a lithium-ion battery and it determines the capacity, cyclic performance and thermal stability of the battery. In order to improve the electrochemical properties of the cathode material, researchers have attempted to modify the cathode surface by using stable materials [1, 2].

The layered transition metal oxide compounds which are composed of hexagonal close packed oxygen atoms network with lithium and transition metal ions in an alternating (111) planes, such as $LiCoO_2$, $LiNiO_2$, $LiCo_xNi_{1-x}O_2$ etc. have been studied extensively as alternate cathode materials for low power applications. Among them, $LiCoO_2$ has found large scale potential applications in the commercial lithium ion batteries. Although intensive investigations have been devoted in finding most cost effective and less toxic alternate materials like $LiMnO_2$, $LiMn_2O_4$ etc., $LiCoO_2$ is still so far the most successful, and reliable choice due to superior

cycling stability and power density. Also it has been widely used as cathode material due to advantages of high specific capacity, high operating voltage, good reversibility, low self-discharge and long cycle life [3-6]. $LiCoO_2$ crystallizes in the layered rock-salt α-$NaFeO_2$ type structure with hexagonal lattice parameters a = 2.815 Å and c = 14.049 Å. The rock salt $LiCoO_2$ lattice consists of a close packed network of oxygen ions with lithium and cobalt ions on alternating (111) planes of the cubic rock salt sublattice. The Co and Li cations occupy the octahedral 3a and 3b sites, respectively, while oxygen anions are located on the 6c sites, The CoO_6 octahedra are shared edges to form CoO_2 sheets and Li ions can move in two dimensional (2-D) directions between the CoO_2 slabs. Due to layered rock-salt structure (R3m) in which a large fraction of lithium ions can be de-intercalated and re-introduced several times without any apparent loss of structural integrity. The growth of this cathode material with preferred hexagonal orientation is of great interest as a result of their possible use in the fabrication of all rechargeable Li-ion batteries.

The growth of $LiCoO_2$ thin films with preferred orientation is known to be crucial. Several thin film deposition techniques such as pulsed laser deposition [7-13], electrostatic spray deposition [14] and chemical vapour deposition [15] were employed for the growth of $LiCoO_2$ thin films. PLD has been widely recognized as a very promising, versatile and efficient method for the deposition of metal oxide thin films [16]. PLD is a powerful and flexible technique for fabricating simple and complex metal oxide films, and has several advantages for thin film deposition: (1). Direct stoichiometry transfer from the target to the growing film. (2). High deposition

rate and inherent simplicity for the growth of multilayered structures. (3). Dense, textured films can be produced more easily by PLD with in situ substrate heating. Fig. 1 shows the schematic diagram of the pulsed laser deposition chamber. 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. In thin film deposition, the oxygen partial pressure plays an important role of determining the structure, surface morphology and vibrational modes of films. The films formed at lower oxygen partial pressures (< 100 mTorr) were sub-stoichiometric. At lower oxygen partial pressures, the degree of ionization is low since the availability of reacting oxygen atoms is low. The plasma is not sustained if the pressure is decreased below 50 mTorr. When the oxygen partial pressure increases, the degree of ionization also increases and hence the reactivity of oxygen ions increases and leads to the formation of stoichiometric films. With increasing pressure, the two Raman modes of $LiCoO_2$ shift to higher frequencies, their absolute intensities increase, the intensity ratio changes and the line widths also vary. So, it appears that the pressure effects on Raman intensities are induced by changes in the electronic structure. Hence in this study, we have presented FTIR, Raman and electrochemical properties of $LiCoO_2$ thin films deposited at higher oxygen partial pressure of 200 mTorr.
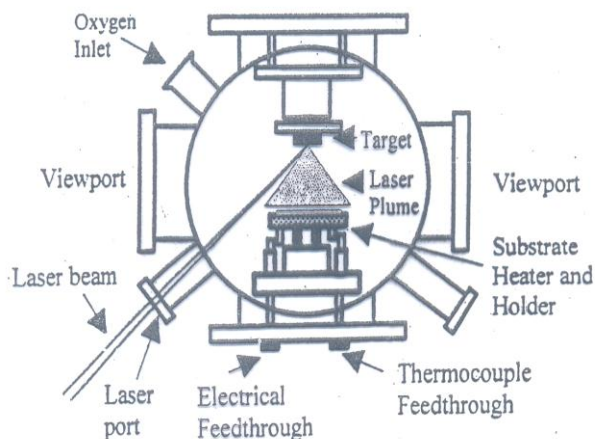

Fig. 1. Schematic diagram of the pulsed laser deposition chamber

2. Experimental

$LiCoO_2$ films were grown by pulsed laser deposition technique. $LiCoO_2$ 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 ^{0}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 248 nm 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 1x3 mm and the energy 300 mJ. The target substrate distance was 4 cm. 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 [17, 18]. FTIR absorption spectra were recorded at room temperature using a Brucker IFS 113v interferometer. 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 electrochemical measurements were also carried out on Li//$LiCoO_2$ cells with a lithium metal foil as anode and $LiCoO_2$ film as cathode of 1.5 cm^2 active area using a Teflon home-made cell hardware.

3. 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. A minimum of 100 mTorr of oxygen partial pressure during the growth is observed to be required to avoid oxygen deficiency in the films. The XRD data revealed that the films have (1 0 1), (0 0 6), (0 1 2), (1 0 4), (0 1 8) and (1 1 0) orientations with predominated (0 0 3) orientation at their relative 2θ positions. The observed X-ray reflecting Bragg angle positions of $LiCoO_2$, corresponding prominent orientations and the inter-planar distances (d) results that the deposited $LiCoO_2$ thin films having hexagonal structure with R3m space group.

3.1 FTIR studies

FTIR absorption spectra were recorded at room temperature using a Brucker IFS 113v interferometer. In the study region (100-1200 cm^{-1}), the spectrometer was equipped with a 3.5 μm-thick beam splitter, a globar source, and a DTGS/PE far –infrared detector. Samples were ground to fine powders painted onto polyethylene slabs. Data were collected in transmission mode at a spectral resolution of 2 cm^{-1} after several scans. FTIR spectra of $LiCoO_2$ thin films have been recorded at various stages of pulsed laser deposition. $LiCoO_2$ possesses the R3m space group, D^5_{3d} spectroscopic symmetry. According to the results of the theoretical factor-group analysis, four modes are active in the infrared spectrum ($2A_{2u}$ & $2E_u$) of the $LiCoO_2$ crystal [19]. Fig. 2 shows the FTIR spectrum of $LiCoO_2$ thin films deposited on silicon substrate maintained at temperature 500 ^{0}C in an oxygen partial pressure pO_2 = 200 mTorr. The spectrum displayed

the characteristic IR dominant bands at 250 and 554 cm^{-1} for $LiCoO_2$. The former is attributed to the asymmetric stretching mode of the octahedral LiO_6 units, while the latter is due to the asymmetric stretching vibration of CoO_6 groups. FTIR features presented in Fig. 2 are in good agreement with elemental analysis [20, 21].
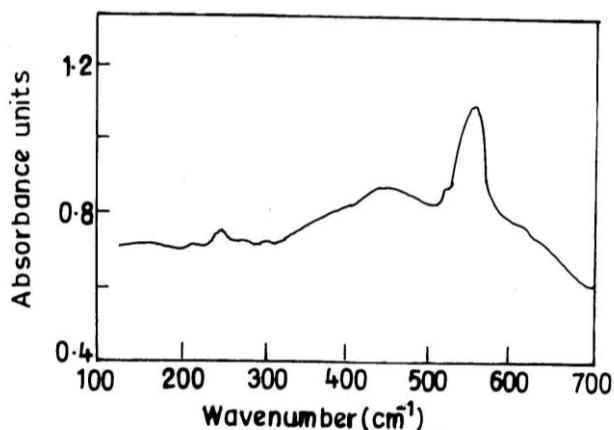

Fig. 2. FTIR spectra of LiCoO₂ thin films deposited in pO₂ = 200 mTorr

3.2 Raman studies

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 514.5 nm 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.

$LiCoO_2$ 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 [19]. Fig. 3 shows non-polarized Raman spectra of thin films deposited in pO_2 = 200 mTorr [22]. The unpolarized Raman scattering spectra of $LiCoO_2$ films deposited on silicon in pO_2 = 200 mTorr showed 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 Raman band located at 592 cm^{-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 484 cm^{-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. These results show that, as expected, the A_{1g} stretching mode should be at higher energy than the E_g bending mode. These results are in good agreement with the results reported by Iriyama et al. [23, 24]. With increasing pressure, the two Raman modes of $LiCoO_2$ shift to higher frequencies, their absolute intensities increase, the intensity ratio changes and the line widths also vary. So, it appears that the pressure effects on Raman intensities are induced by changes in the electronic structure. The difference in the Li-O and Co-O bond compressibilities affects the distortions of the octahedral coordinations. With increasing pressures, the difference in O-O distances become smaller and the bond angles change. The CoO_6 octahedra undergo corresponding changes. So, the distortions in both types of octahedral are reduced when applying pressure.
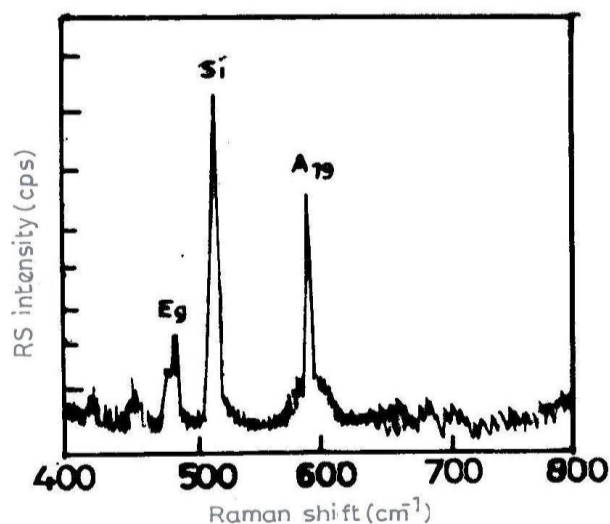

Fig. 3. Raman spectra of LiCoO₂ thin films deposited in pO₂ = 200 mTorr

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 [19].

3.3 Electrochemical studies

The electrochemical measurements were carried out on Li//LiCoO$_2$ cells with a lithium metal foil as anode and LiCoO$_2$ film grown at 500 ^{0}C in an oxygen partial pressure of 200 mTorr as cathode of 1.5 cm^2 active area using a Teflon home-made cell hardware. The silicon substrate was mounted on Ag wire with silver paint and covered by insulating epoxy leaving only the PLD film as active area. The electrolyte consisted of 1 M LiClO$_4$ dissolved in propylene carbonate. Typical charge discharge curves of Li//LiCoO$_2$ cells using pulsed laser deposited film grown at temperature 500 ^{0}C in an oxygen partial pressure of 200 mTorr are shown in Fig. 4. Electrochemical measurements were carried out at a rate of C/100 in the potential range 2.0 - 4.2 V; as such, the voltage profile should provide a close approximation to the open circuit voltage (OCV). From the electrochemical features, we may make some general remarks that are (1) an initial voltage about 2.15 V versus Li/Li$^+$ was measured for LiCoO$_2$ thin film cathode cells, which is lower to that recorded in the galvanic cell using crystalline cathode [25, 26], (2) the cell voltage profiles display the typical profile currently observed for Li$_x$CoO$_2$ cathodes. The incremental capacity curve (-δx/δV) versus cell voltage for the Li//LiCoO$_2$ thin film cell that is derived from the charge curve exhibited only one well defined voltage, which displayed a peak centered at 3.65 V. The electrochemical process seems to be a classical intercalation mechanism for the lithium ions into the Li$_x$CoO$_2$ matrix as indicated by the peak. These results suggest that about 0.5 Li can be removed at charge potential up to 4.2 V. In the high voltage region, such a cell delivered a specific capacity of 185 mC/cm^2 μm [27, 28].
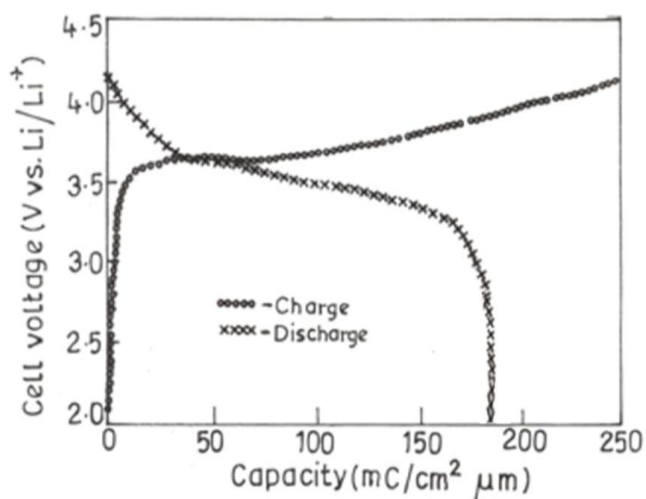

Fig. 4. Charge-discharge profile of Li//LiCoO$_2$ cells deposited in pO$_2$ = 200 mTorr

4. Conclusion

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 FTIR spectrum displayed the characteristic IR dominant bands at 250 and 554 cm^{-1} for LiCoO$_2$. The former is attributed to the asymmetric stretching mode of the octahedral LiO$_6$ units, while the latter is due to the asymmetric stretching vibration of CoO$_6$ groups. The Raman data consist of a series of broad bands located between 400 and 700 cm^{-1} for LiCoO$_2$ films. The Raman band located at 592 cm^{-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. The RS peak at 484 cm^{-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 Li//LiCoO$_2$ cells were tested in the potential range 2.6 – 4.2 V. Specific capacity 185 mC/cm^2 μm was measured for the film grown at at 500 ^{0}C in an oxygen partial pressure of 200 mTorr. 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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