

Raman investigations on laser ablated LiCoO_2 and $\text{LiTi}_x\text{Co}_{1-x}\text{O}_2$ thin film cathodes

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Thin films of LiCoO_2 and $\text{LiTi}_x\text{Co}_{1-x}\text{O}_2$ were prepared by pulsed laser deposition technique. Raman studies were performed with respect to their deposition parameters i.e. substrate temperature (T_s), oxygen partial pressure ($p\text{O}_2$) and target composition in the deposition chamber. The Raman data consist of a series of broad bands located between 400 and 700 cm^{-1} for LiCoO_2 and $\text{LiTi}_x\text{Co}_{1-x}\text{O}_2$ 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. The RS peak position at 484 cm^{-1} derives from the E_g species. The symmetric motions involve Co-O stretching and O-Co-O bending vibrations. The I_{484}/I_{592} increased with a decrease in the degree of the c-axis orientation of the films. The film deposited at 700 °C in $p\text{O}_2 = 100$ mTorr, indicating that the film had no preferred orientation. The Raman peaks observed for the $\text{LiTi}_x\text{Co}_{1-x}\text{O}_2$ films at 594 cm^{-1} and 485 cm^{-1} are ascribed to Raman active modes A_{1g} and E_g respectively. The Raman modes are observed to be slightly broader than that of pure LiCoO_2 films due to polyhedra distortion in pristine LiCoO_2 , indicating the incorporation of Ti into Co sites. The influence of titanium doping on the Raman peaks has been systematically studied.

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1. Introduction

Recently, thin films of functional materials including oxide ceramics have become important for use in many electronic, photonic, magnetic, ionic, etc., devices. Fabrication of the materials as thin film cathodes for application in all solid state microbatteries has been another interesting field of research owing to the miniaturization and the reduced power consumption of many kinds of electronic devices. Due in large part to high-energy storage capacity, LiCoO_2 is the prototypical positive electrode material for lithium ion batteries. The increasing interest of LiCoO_2 thin films comes both from the technological application in all-solid-state microbatteries and the fundamental studies of lithium intercalation process into the oxide matrix [1, 2]. LiCoO_2 crystallizes in the layered rock-salt $\alpha\text{-NaFeO}_2$ type structure with hexagonal lattice parameters $a = 2.815$ Å and $c = 14.049$ Å [1].

LiCoO_2 is considered to have high specific density, high voltage, long cycle life and good reversibility for lithium intercalation – deintercalation process. It is easy to prepare but its high cost and toxicity remain problems to be solved. Preparation of titanium doped LiCoO_2 films may have advantages from a point of view of fundamental studies (because it is a binder free material with a well-defined interfacial area) and of the emerging field of microbatteries as well. Doping with non-transition metals such as titanium has gained increasing interest for the following reasons: (1) the low cost and low toxicity, (2) the fact that titanium substitution for transition metal oxides leads to higher lithium intercalation voltages, (3) the titanium doping stabilizes the layered structure and

extends the cyclability and enhances the capability of the electrochemical cells. The growth of LiCoO_2 thin films with preferred orientation is known to be crucial. Various aspects of LiCoO_2 thin films prepared by RF sputtering [3, 4], pulsed laser deposition [4-8], electrostatic spray [9], and chemical vapour deposition [10], have been reported.

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. Another chief advantage is, PLD films crystallize at relatively low deposition temperatures than the other physical vapour deposited films. Iriyama et al., [6] prepared thin films of LiCoO_2 by PLD and studied the electrochemical performance. However the investigations on the Raman spectroscopic features of the films that are essentially depend upon the deposition parameters give a scope for effective utilization of these thin films in the fabrication of microbatteries. In this paper, we present Raman studies of LiCoO_2 and $\text{LiTi}_x\text{Co}_{1-x}\text{O}_2$ films deposited on silicon substrates using the PLD technique from a sintered target.

2. Experimental

LiCoO_2 and $\text{LiTi}_x\text{Co}_{1-x}\text{O}_2$ were prepared by pulsed laser deposition technique on silicon substrates. 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. $\text{Li/Co} > 1.0$ by adding Li_2O , whereas for titanium

doped films the target was prepared by sintering a mixture of high purity LiCoO_2 and Ti powders (Cerac products) with excess of Li i.e., $\text{Li/Co} + \text{Ti} = 1.1$ by adding Li_2O . The mixture was crushed, pressed and sintered at 800°C to get quite robust targets and used for the growth of films. 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 1×3 mm and the energy 300 mJ. The power density at the target surface was 10 Jcm^{-2} . 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 [12].

The Raman spectra of the 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 .

3. Results and discussion

Pulsed laser deposited LiCoO_2 and $\text{LiTi}_x\text{Co}_{1-x}\text{O}_2$ films are pin-hole free as revealed from optical microscopy and well adherent to the substrate surface. The thicknesses of LiCoO_2 and $\text{LiTi}_x\text{Co}_{1-x}\text{O}_2$ films are 250 nm. The influence of oxygen partial pressure ($p\text{O}_2$) and deposition temperature (T_s) on the Raman studies were systematically studied.

3.1 Raman studies on LiCoO_2 films

LiCoO_2 possesses the $R3m$ space group, D_{3d}^{53d} 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]. Fig. 1(a-c) shows the unpolarized Raman scattering spectra of LiCoO_2 films deposited on silicon maintained at 300°C in oxygen partial pressure $p\text{O}_2 = 100 \text{ mTorr}$ as a function of the target composition.

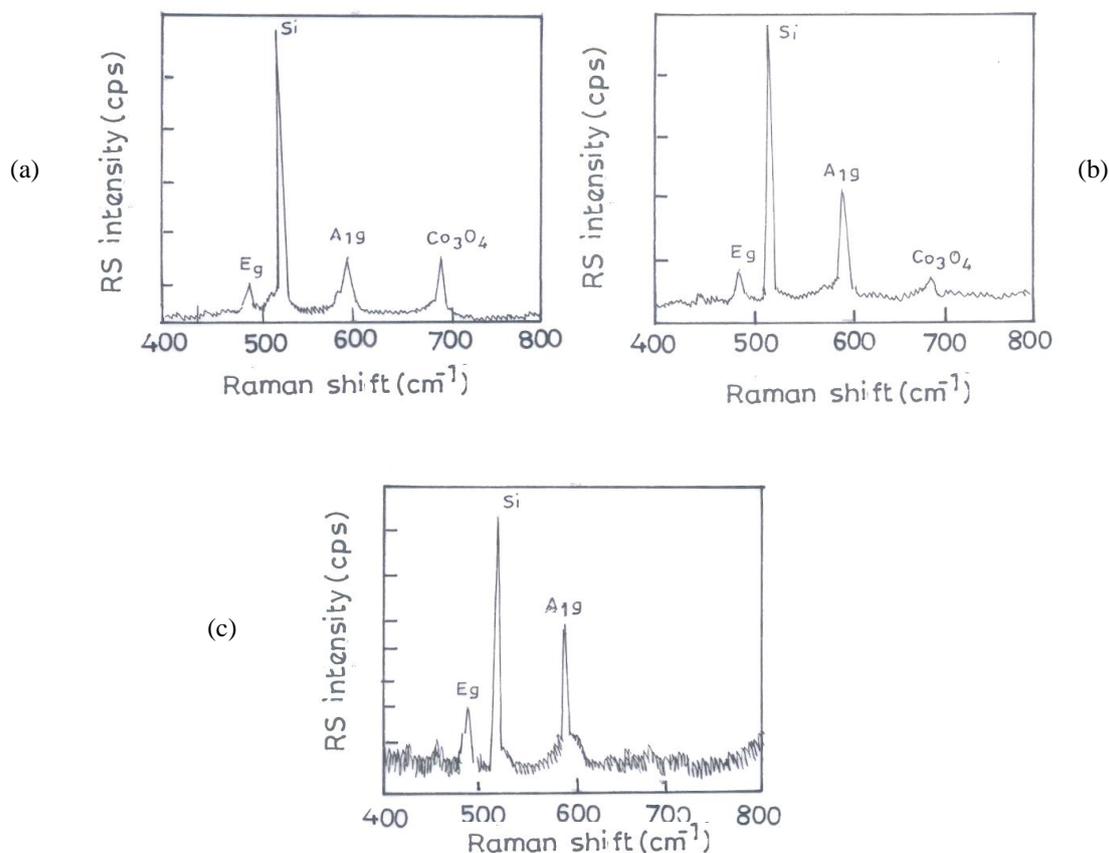


Fig. 1. Raman spectra of LiCoO_2 thin films deposited from composite target with different concentrations of Li_2O : (a) without Li_2O (b) 10 wt.%, and (c) 15 wt.%.

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} [14]. 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 [15]. The vibrational signature of the LiCoO_2 matches well the two allowed Raman modes. The peak located at 693 cm^{-1} in Raman spectra (Fig. 1(a) and (b)) indicates the presence of Co_3O_4 impurities in the film [16]. 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 Fig. 1(b-c). Upon addition of Li_2O , the peak at 693 cm^{-1} decreased substantially indicating the disappearance of Co_3O_4 species as it is shown in the RS spectra (Fig. 1(c)). The optimum concentration of Li_2O to compensate the lithium loss must be 15% of Li_2O . LiCoO_2 possess the prototype symmetry $R\bar{3}m$ 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 [16]. 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 [15]. 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_{3d}^{5d} 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 [14].

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 592 cm^{-1} correspond to the E_g and A_{1g} optical modes of LiCoO_2 , respectively [15]. 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 $\text{Li}_2\text{O} \leq 15\%$, 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 ($T_s > 300\text{ }^\circ\text{C}$), and oxygen partial pressure ($p\text{O}_2 = 100\text{ mTorr}$) promotes reconstruction of the stoichiometric LiCoO_2 layered framework [12, 14].

Raman spectroscopy is also useful to distinguish between different symmetries in a given material. Fig. 2 shows non-polarized Raman spectra of thin films deposited at different temperatures in $p\text{O}_2 = 100\text{ mTorr}$. The spectra are nonpolarized by the intensity of the A_{1g} peak at 592 cm^{-1} . I_{484} and I_{592} are referred as intensities of the E_g and A_{1g} bands respectively. The I_{484}/I_{592} increased with a decrease in the degree of the c-axis orientation of the films. The film deposited at $700\text{ }^\circ\text{C}$ in $p\text{O}_2 = 100\text{ mTorr}$, indicating that the film had no preferred orientation. These results are in good agreement with the results reported by Iriyama et al. [6, 14].

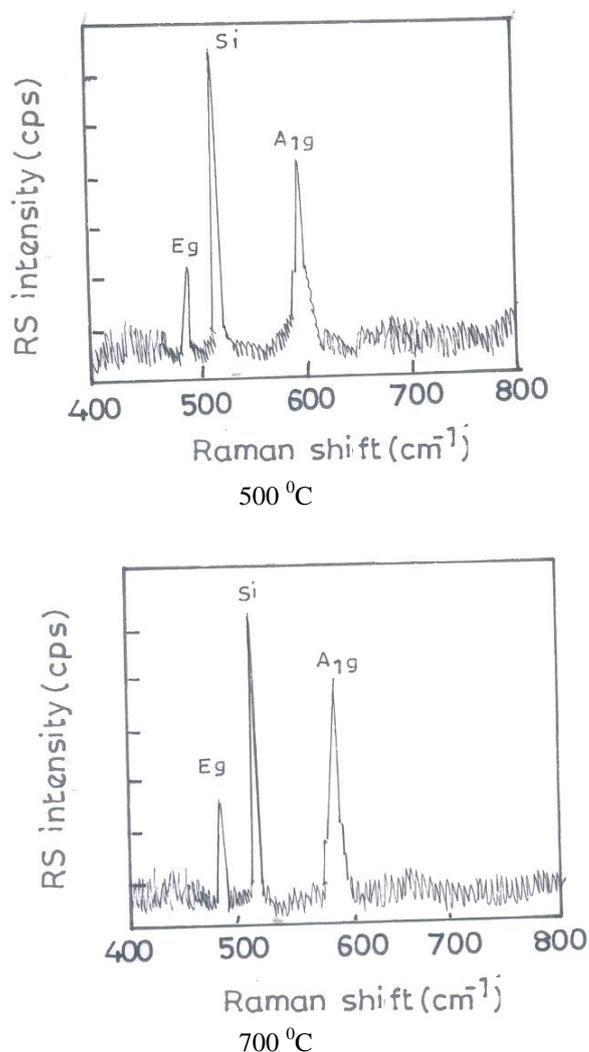


Fig. 2. Raman spectra of LiCoO_2 thin films deposited at different substrate temperatures in $p\text{O}_2 = 100\text{ mTorr}$

3.2 Raman studies on $\text{LiTi}_x\text{Co}_{1-x}\text{O}_2$ films

Fig. 3 [12] shows the Raman spectra of titanium doped LiCoO_2 thin films deposited on silicon maintained at temperature in the range 500-700 °C in an oxygen partial pressure $p\text{O}_2 = 100$ mTorr. The titanium doped LiCoO_2 has a layered structure and the atoms (Co, Li and O) are located in the Wyckoff sites 3a, 3b and 6c respectively. The Raman peaks observed for the films at 594 cm^{-1} and 485 cm^{-1} are ascribed to Raman active modes A_{1g} and E_g respectively. Since the Raman modes are entirely due to oxygen atoms, hence the symmetric motions involve Co-O stretching and O-Co-O bending vibrations. These Raman modes are observed to be slightly broader than that of pure LiCoO_2 films due to polyhedra distortion in pristine LiCoO_2 , indicating the incorporation of Ti into Co sites. It is clearly seen from the Raman spectra that the grown films have no impurity peaks [12].

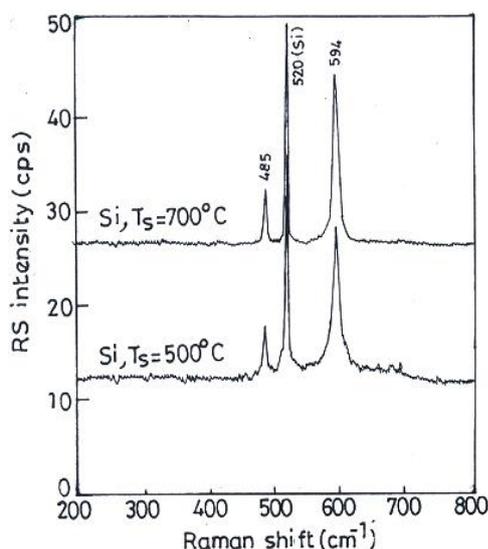


Fig. 3. Raman spectra of titanium doped LiCoO_2 films deposited at different substrate temperatures in $p\text{O}_2 = 100$ mTorr

4. Conclusions

Thin films of LiCoO_2 and $\text{LiTi}_x\text{Co}_{1-x}\text{O}_2$ 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 592 cm^{-1} can be viewed as the symmetric Co-O stretching vibration of CoO_6 groups. The RS peak position at 484 cm^{-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 Raman peaks observed for the $\text{LiTi}_x\text{Co}_{1-x}\text{O}_2$ films at 594 cm^{-1} and 485 cm^{-1} are ascribed to Raman active modes A_{1g} and E_g respectively. These results suggest that the open and porous structured LiCoO_2 and $\text{LiTi}_x\text{Co}_{1-x}\text{O}_2$ thin films find potential applications as binder free electrode in the fabrication of all solid state microbatteries.

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