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Influence of oxygen partial pressure on optical absorption and electrical conduction behavior of $LiCoO_2$ thin films

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$LiCoO_2$ thin films were prepared by pulsed laser deposition technique (PLD) in the partial pressure rage 50-300 mTorr. The optical absorbance of $LiCoO_2$ thin films have been studied in the vicinity of the fundamental absorption edge at substrate temperature of 600 ^{0}C in relation to the oxygen partial pressure. A gradual increase of the optical transmission from 400 to 1000 nm with the appearance of a prominent dip at 750 nm is observed. This feature is pronounced for the crystallized film grown in oxygen partial pressure of 200 mTorr. The variation of the optical absorption near the fundamental edge allows determining the energy gap between d-bands of $LiCoO_2$. Band gap energies of 2.36 and 2.28 eV for films grown in $pO_2 = 50$ mTorr and $pO_2 = 200$ mTorr, respectively, with accuracy ± 0.02 eV were measured. Increment in oxygen partial pressure leads to an increase of the electrical conductivity of order of magnitude from 8×10^{-7} S/cm to 2×10^{-7} S/cm for $LiCoO_2$. The increase of electrical conductivity could be connected with the decrease of the activation energy. These results suggest that the open and porous structured $LiCoO_2$ films find potential applications as binder free electrode in the fabrication of all solid state microbatteries.

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Keywords: $LiCoO_2$ thin films, PLD, Optical, Band gap, Electrical, Activation energy

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1. Introduction

With the tendency in microelectronics towards further decrease in the size of active elements the critical distribution of electric power becomes a major limitation for further integration. This can be avoided by the use of integrated solid state microbatteries to provide local power. 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. $LiCoO_2$ is considered to have high specific density, high voltage, long cycle life and good reversibility for lithium intercalation – deintercalation process [1, 2].

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 rock - salt sublattice. 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 there by 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 [1, 3-6], pulsed laser deposition [3, 7-11], electrostatic spray deposition [12] and chemical vapour deposition [13, 14] 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 [15]. In particular, it has been successfully employed for the deposition of simple and complex metal oxide materials with desired composition, structure, physical and chemical properties. Fig. 1 represents 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. Another chief advantage is, PLD films crystallize at relatively low deposition temperatures than the other physical vapour deposited films. In addition, PLD is environmentally friendly. In addition to oxides, PLD has also been effective in growing nitride films in nitrogen ambient, multilayered structures such as superconductors and ferroelectric memory devices. PLD is also known for its fast turn around time when growing a thin film of a new material starting from its powder form.

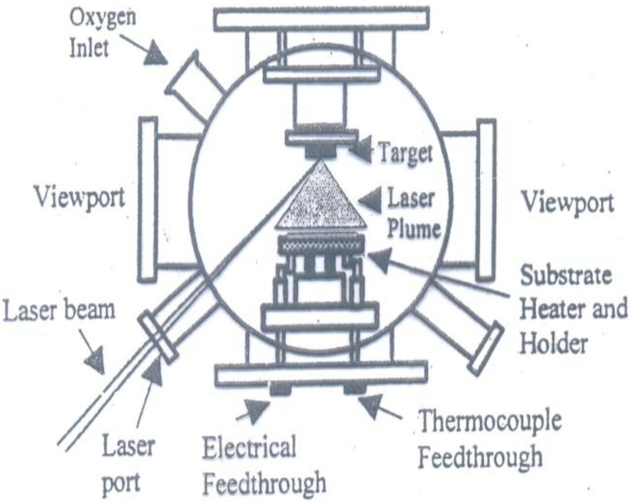

Fig. 1. Schematic diagram of the pulsed laser deposition chamber

The electronic structure of the Co-3d bands of layered rock salt $LiCoO_2$ consists of three Co-t_{2g} (valence bands) and two Co-e_g (conduction bands). Theoretical investigations have shown that the Co-e_g bands are empty and their peak position lies at around 1.7 eV above the top to the Co-t_{2g} bands [16]. The density of states due to the Co-e_g bands consist of a prominent peak at ~2.2 eV above the Fermi level E_F in the Co-t_{2g} band [17]. Poly-crystalline layered R3m phase thin films of $LiCoO_2$ were grown by PLD by Julien et al. [18]. Hence in the present study the influence of oxygen partial pressure on the optical and electrical properties of pulsed laser deposited $LiCoO_2$ thin films were reported.

2. Experimental

$LiCoO_2$ films were grown 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. Li/Co > 1.0 by adding Li_2O. The mixture was crushed and pressed at 5 tonns.cm^{-2} to make tablets of 2 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. quartz glass 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 [19-21].

The optical properties of $LiCoO_2$ thin films are recorded using Hitachi U 3400 UV-VIS-NIR double beam spectrophotometer with accuracy limits ± 0.2 nm in the UV- VIS region and ± 1 nm in the NIR region. The dc electrical conductivity measurements are made on the $LiCoO_2$ thin films employing the standard four-probe technique.

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 thicknesses of $LiCoO_2$ films are 250 nm. The influence of oxygen partial pressure (pO_2) and deposition temperature (T_s) on the optical and electrical properties were systematically studied.

3.1. Optical properties

The study of optical absorption, particularly the absorption edge, has proved to be very useful for elucidation of the electronic structure of the materials. It is possible to determine whether the optically induced transition is direct or indirect and allowed or forbidden by analysis of the absorption edge.

The optical absorption coefficient of the films is evaluated using the relation

$$\alpha = 1/t \ln (T/(1-R)^2) \tag{1}$$

where T is the transmittance, R is the reflectance and t the thickness of the film.

For incident photon energy greater than the band gap and above the exponential tail the optical absorption follows a power law of the form

$$\alpha(hv) = B(hv - E_g)^n \tag{2}$$

where B is a constant, E_g is the band gap of the material and n is the exponent. The exponent n determines the type of electronic transition causing the absorption and take the values 1/2, 3/2, 2 and 3 for direct allowed, direct forbidden, indirect allowed and indirect forbidden transitions respectively [22].

The optical absorbance of $LiCoO_2$ thin films have been studied in the vicinity of the fundamental absorption edge. Fig. 2 shows the transmission spectra of thin films deposited at T_s =600 ^{0}C in the wavelength range 300-1200 nm as a function of the oxygen partial pressure. We observed a gradual increase of the optical transmission from 400 to 1000 nm with the appearance of a prominent dip at 750 nm. This feature is more pronounced for the well-crystallized film grown in pO_2 = 200 mTorr. Plots of the optical absorbance, $(\alpha h\nu)^2$ versus photon energy for $LiCoO_2$ films are shown in Fig. 3. The variation of the optical absorption near the fundamental edge allows to determine the energy gap between d-bands of $LiCoO_2$. These plots gave the band gap energy of 2.36 and 2.28 eV for films grown in pO_2 = 50 mTorr and pO_2 = 200 mTorr, respectively, with accuracy ± 0.02 eV [19-21].

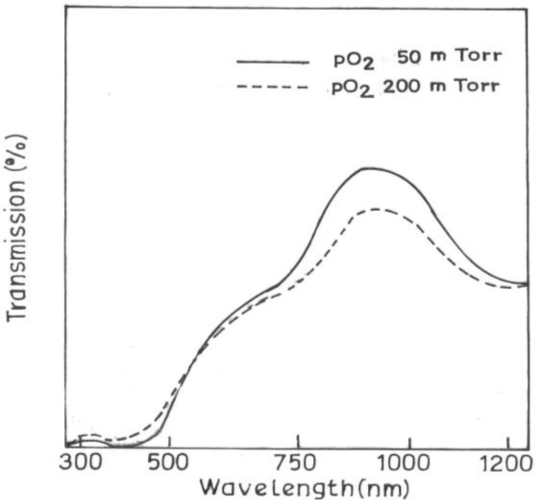

Fig. 2. Optical transmission spectra of $LiCoO_2$ films deposited at different oxygen partial pressures

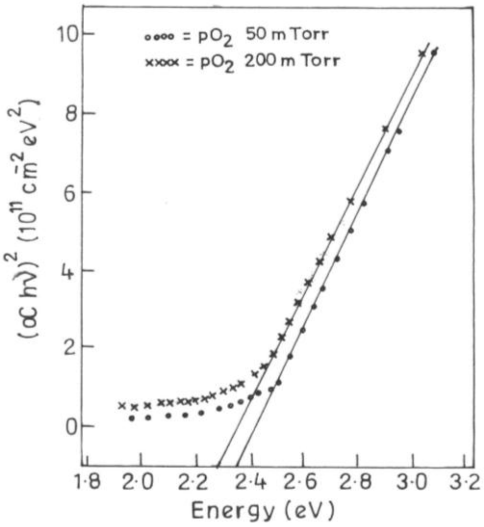

Fig. 3. Plot of the optical absorbance, $(\alpha h\nu)^2$ vs. hν, for $LiCoO_2$ films deposited at different oxygen partial pressures

The electronic structure of the Co-3d bands of layered rock salt $LiCoO_2$ consists of three Co-t_{2g} (valence bands) and two Co-e_g (conduction bands). Theoretical investigations have shown that the Co-e_g bands are empty and their peak position lies at around 1.7 eV above the top to the Co-t_{2g} bands [16]. The density of states due to the Co-e_g bands consist of a prominent peak at ~2.2 eV above the Fermi level E_F in the Co-t_{2g} band [17]. The experimental data of optical absorption related to Co-3d bands in $LiCoO_2$ have been also reported [22]. Excess of Li in $LiCoO_2$ increases the Co-O bond length leading to a small σ overlap between the O-2p and Co-3d orbitals, thereby pushing the antibonding bands (e_g bands) down [17]. Thus the textured films allowed for investigation of the d-d electronic transition in $LiCoO_2$. Our experimental data that is optical absorption support the above theoretical prediction [19-21].

3.2. Electrical properties

Electrical transport plays an important role in the performance of the electrode in lithium microbattery. According to the electronic considerations [23], the small polaron semiconducting character of the $LiCoO_2$ compound is due to weak M-M interactions, which prevents an itinerant-electron bandwidth giving localized electronic configurations. Fig. 4 shows the temperature dependence of the dc conductivity for $LiCoO_2$ thin films at different partial pressures. These Arrhenius plots for the electrical conductivity showed that the conduction is thermally activated owing to the semiconducting character of these oxides. Upon increasing the oxygen partial pressure, we clearly observed a subsequent increase of the conductivity of $LiCoO_2$ film.

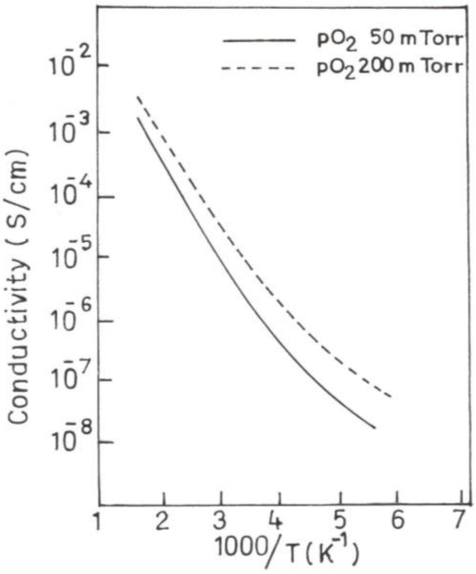

Fig. 4. Arrhenius plots of $LiCoO_2$ thin films deposited at different oxygen partial pressures

The electrical conductivity of $LiCoO_2$ varies from 10^{-9} to 10^{-4} S/cm in the temperature range from 180 to 500 K. Increment in oxygen partial pressure leads to an increase of the electrical conductivity of order of magnitude from 8 x 10^{-7} S/cm for the film grown in pO_2 = 50 mTorr to 2 x 10^{-7} S/cm for the film grown in pO_2 = 200 mTorr. The increase of electrical conductivity could be connected with either an enhancement in the effective carrier concentration or a decrease of the activation energy with increase of partial pressure. Examination of the data (Fig. 4) indicates that a noticeable change in the activation energy is observed in the temperature range 250–500 K. The activation energy decreases from 0.34 eV to 0.26 eV on increasing the partial pressure [19, 20]. In fact, the conduction in the semiconducting $LiCoO_2$ phase imposes Co^{4+} and Co^{3+} ions, which allows for facile transfer of charge carriers via hopping. Thus the electrical conductivity of lithium cobaltates with the layered structure ought to depend on the valencies of the cations and their distribution among the crystallographic positions in the framework. The curvature appearing in the

Arrhenius plots of σ_{dc} at temperature around 280 K suggests the possibility of a variable range hopping mechanism for the small polaron transport [23].

4. Conclusions

$LiCoO_2$ thin films were grown using the pulsed laser deposition technique, in which the control of the deposition parameters promotes the film stoichiometry. PLD films were found to be uniform with regard to the surface topography, thicknesses and well adherent to the substrate surface. The optical absorbance of $LiCoO_2$ thin films have been studied in the vicinity of the fundamental absorption edge with respect to oxygen partial pressure. A gradual increase of the optical transmission from 400 to 1000 nm with the appearance of a prominent dip at 750 nm is observed. The variation of the optical absorption near the fundamental edge allows determining the energy gap between d-bands of $LiCoO_2$. Band gap energies of 2.36 and 2.28 eV for films grown in $pO_2 = 50$ mTorr and $pO_2 = 200$ mTorr, respectively, with accuracy ± 0.02 eV were measured. Increment in oxygen partial pressure leads to an increase of the electrical conductivity of order of magnitude from 8×10^{-7} S/cm to 2×10^{-7} S/cm for $LiCoO_2$. The increase of electrical conductivity could be connected with the decrease of the activation energy. These results suggest that the open and porous structured $LiCoO_2$ films find potential applications as binder free electrode in the fabrication of all solid state microbatteries.

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