Growth of nano-structured TiO_2-doped $LiCoO_2$ PLD films and their structural and optical properties

O.M. Hussain[a], M.C. Rao[a], and C.M. Julien[b]
[a]Thin Film Laboratory, Department of Physics
S.V. University, Tirupati 517502, India
[b]LMDH, UMR 7603, Université Pierre et Marie Curie
4 place Jussieu, 75252 Paris cedex 05, France

Due in large part to its high energy storage capacity, $LiCoO_2$ is the prototypical positive electrode material for Li-ion batteries. The increasing interest of $LiCoO_2$ thin films comes from both the technological application in all-solid-state micro-batteries and the fundamental studies of lithium intercalation process.

$LiCoO_2$ films doped with 10%TiO_2 were grown on various substrate materials using the pulsed laser deposition (PLD) technique from target sintered at 850°C. Films were deposited over the substrate temperature range 500°C≤Ts≤700°C and in the oxygen partial pressure range 100 mTorr≤P(O_2)≤200 mTorr. PLD films were subsequently characterized with respect to their composition (RBS analysis), their structure (XRD, Raman and FTIR spectroscopy) and their morphology (AFM).

XRD patterns show that $LiCoO_2$ films deposited on silicon substrate have a preferred (003) orientation. The structure corresponds to that of the rhombohedral α-$NaFeO_2$-type (R-3m S.G.).

AFM studies reveal the nano-structured morphology of the films (Fig. 1). $LiCoO_2$ PLD films grown at Ts=600°C are well textured. The influence of TiO_2 doping on particle size and morphologies has been clearly evidenced.

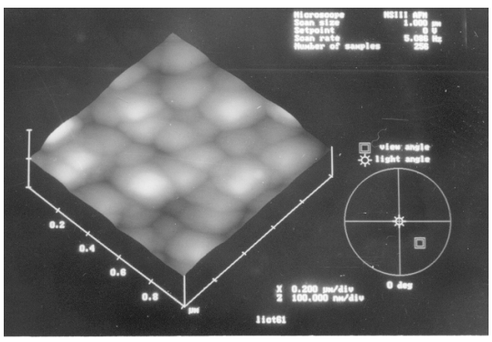

FIG. 1.

FTIR absorption spectra indicate the layered local structure related to the short-range environment of oxygen coordination around the cations in oxide lattice. The presence of Li ions in octahedral *3b* sites is evidenced by the low-wavenumber band at ca. 250 cm^{-1}, which is attributed to the asymmetric stretching mode of octahedral LiO_6 units (Fig. 2). The Raman scattering (RS) spectra show the characteristic features at ca. 485 and 595 cm^{-1} as expected for layered $LiCoO_2$. However, additional peaks attributed to the presence of Co_3O_4 impurities are observed in RS spectra of PLD films grown at low temperature (Ts=500°C, P(O_2)=100 mTorr).

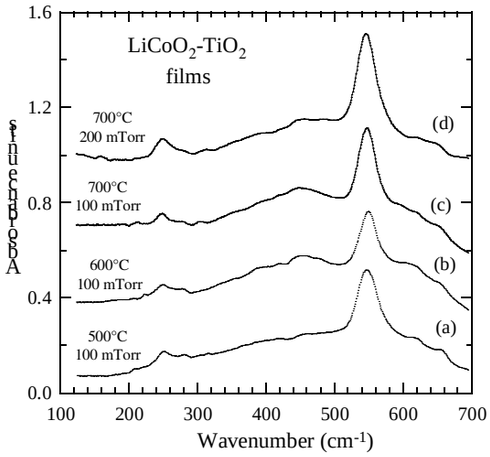

FIG. 2.

Optical absorption was studied in the visible region to determine transitions associated with the peak energy of the density of states for the conduction band. A prominent fundamental absorption was observed at 2.3 eV above the Fermi level which is attributed to the d→d transition from E_F in the Co(t_{2g}) band to the Co(e_g) in $LiCoO_2$. The energy of this transition appears to be sensitive to the crystallinity of the film.