

Highly Oriented Growth of Pulsed-Laser Deposited $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ Films for Application in Microbatteries

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There is a constantly increasing demand for miniaturized high energy density batteries to power microsystems such as microsensors, smart cards, implantable medical devices, intelligent labels, and so on.^{1,2} The tremendous recent interest in the development of solid-state rechargeable lithium microbatteries has generated a strong interest in synthesis and characterization of transition metal oxides in view of their potential application as cathode materials.^{1–10} Several transition metal oxides such as LiCoO_2 , LiNiO_2 , LiMn_2O_4 , and their derivatives have been considered and extensively studied in recent years.^{1–10} Following the early discovery of lithium intercalation properties by Goodenough et al.,¹¹ LiCoO_2 has been exploited and is currently the material employed in commercially available rechargeable batteries.^{5,7,12} However, LiCoO_2 is expensive and toxic. Only 50% of the theoretical capacity could be utilized in the voltage range of 3–4.25 V. Furthermore, LiCoO_2 undergoes a lattice expansion, during charging, along the *c* axis and the oxygen is expelled out from the lattice as a result of the interaction of the electrode surface with electrolyte.⁹ LiNiO_2 has been

considered as an alternative, but the serious problems involved with the material are the synthesis, stoichiometry, structural stability, and poor cyclic performance.¹³ From this viewpoint and to improve the electrochemical properties, the materials research community has conducted rigorous research to develop alternative materials based on the substitution of metal ions into these systems, such as the solid solution systems based on Co and Ni oxides.

The $\text{LiNi}_{1-y}\text{Co}_y\text{O}_2$ ($0 < y < 1$) system, which belongs to the solid solution of LiCoO_2 – LiNiO_2 , has been considered as an attractive choice for developing stable cathode materials for electrochemical applications. The particular composition $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ is expected to form the next-generation electrode material after LiCoO_2 .^{10,14} Because the electrochemical performance is governed by the microstructure of the electrodes, the controlled growth, structure, and fundamental understanding of the factors governing the growth behavior of these oxide materials is highly important. Improved understanding of the synthesis processes and correlation of electrochemical properties with structures enhances our ability to engineer the microstructure and stability and to tune the conditions to produce low-dimensional oxides with excellent properties and enhanced performances. Furthermore, thin film preparation of $\text{LiNi}_{1-y}\text{Co}_y\text{O}_2$ ($0 < y < 1$) system with controlled structure and desired properties is very difficult using conventional evaporation methods because of loss of either lithium or oxygen during deposition.^{15–17} Several post-deposition methods were also proposed to improve the crystallinity or homogeneity of the oxide films.¹⁸ In this context, we have made an attempt to produce $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ films using pulsed-laser deposition (PLD). PLD is a flexible and powerful technique and has been successfully employed in the past for the deposition of a wide variety of materials.^{3,4,8,15,19} The excellent capability of PLD for reactive deposition and to transfer the original stoichiometry of the bulk target to the deposited film makes it suitable for the fabrication of simple and complex metal oxide films.^{3,4,8,15,19}

The impetus for this work is to produce $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ films and to understand their microstructure as a function of growth conditions. The emphasis is not only the fundamental understanding but also the optimization of growth and structure of the PLD $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ films for their application in microbatteries. In this communication, we report on the oriented growth of PLD $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ films with excellent structural stability for integration into micro-battery device technology.

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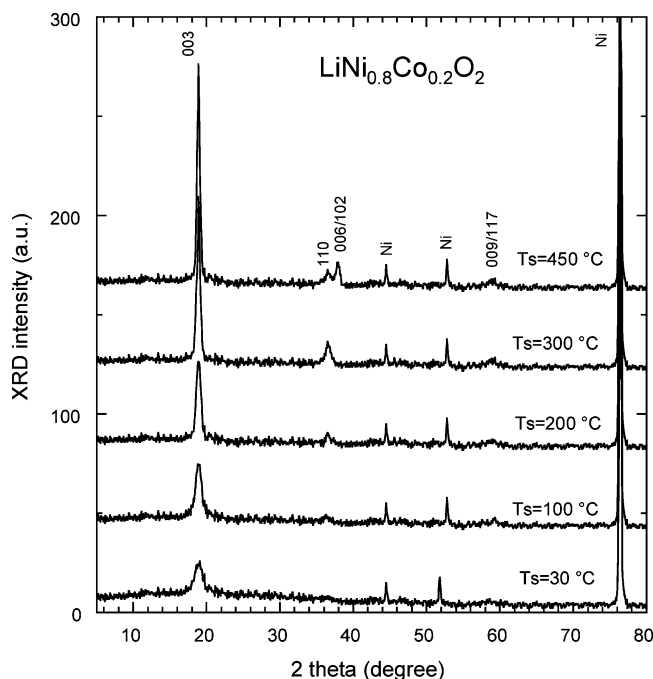


Figure 1. XRD spectra of pulsed-laser deposited $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ films as a function of growth temperature. The oriented growth of $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ films can be noticed. The peaks due to the $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ film and Ni substrate are indexed. The spectra represent the films grown onto Ni metal foil as the substrate was maintained in the temperature range $30 \leq T_s \leq 500$ °C in an oxygen partial pressure of 100 mTorr. A lithium-rich (15 mol % Li_2O) sintered target was used for laser ablation.

$\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ films were prepared by multipulse laser ablation of the targets in the PLD chamber. The targets for PLD were prepared from powders pressed at 1.5–5 ton/cm² and sintered at 800 °C for 24 h. Lithium-rich targets were optimized for 15 mol % Li_2O . The targets were then introduced into the deposition chamber for laser ablation to produce films. The target to substrate distance was 4 cm. The films were deposited onto nickel substrates. The substrate temperature (T_s) was varied in the range room temperature to 500 °C during deposition. The target was rotated at the rate of 10 rotations/min during ablation process to avoid depletion of the material at the same spot and to obtain uniform films. In addition, preliminary pulses were applied using the shutter to eliminate the contamination. The energy and the repetition rate of the laser pulse were 300 mJ and 10 Hz, respectively. The chamber base pressure was 1×10^{-6} Torr prior to deposition. The PLD chamber was backfilled with pure oxygen to the total pressure ($p(\text{O}_2)$) maintained in the range 50–150 mTorr during deposition. The thickness of the PLD $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ films was 1 μm . X-ray diffraction (XRD) patterns of PLD $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ films were carried out using a Philips X'Pert PRO MRD (PW3050) diffractometer equipped with a Cu anticathode (Cu $K\alpha$ radiation $\lambda = 1.54056$ Å) at room temperature.

The XRD patterns of PLD $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ films are shown in Figure 1 as a function of growth temperature. The oxygen partial pressure for all these films was $p(\text{O}_2) = 100$ mTorr. The XRD of $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ films fabricated at RT exhibits the diffuse patterns indicating the amorphous nature of the grown layers. The typical peaks of the crystalline phase began to appear upon increasing the temperature ($T_s > 200$

°C) keeping the oxygen partial pressure at $p(\text{O}_2) = 100$ mTorr and using a lithium-rich target for ablation. This observation is similar to the growth behavior of LiCoO_2 , where the crystalline phase began to appear at $T_s \geq 200$ °C.¹⁵ The XRD pattern of the PLD grown $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ films using a target without a Li_2O additive displayed peaks due to the presence of a secondary phase, which is identified as Co_3O_4 (not shown). XRD patterns show features expected for the regular $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ layered phase when the Li_2O amount in the target used laser ablation is increased to 15 mol %. The important characteristic of the XRD spectra shown in Figure 1 is the absence of any secondary phase such as either NiO or Co_3O_4 , which is usually expected for films formed with lithium deficiency. This is a clear indication of the phase stability of the PLD grown $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ films without any secondary phase growth. The 2θ values of all reflections observed match those in the indexed in the $R\bar{3}m$ system. The peaks due to Ni substrate are as indicated in the figure.

The dominant and intense peaks observed in the XRD spectra are assigned to the (00 l) reflections, which indicate highly oriented growth of the $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ lattice structure. Jang et al. have reported the growth of crystalline LiCoO_2 films with preferred orientation using radio frequency (rf) sputtering onto silicon substrates.²⁰ The highly oriented texture of the rf-sputtered films is attributed to the tendency to minimize volume strain energy at the film–substrate interface and/or to minimize the surface energy at the surface of the films.²⁰ However, the (110) lattice plane reflection showed the highest intensity in the case of the rf-sputtered film while in the case of the PLD film the (003) reflection showed the highest intensity. This orientation with the (00 l) intense reflections corresponds to the c axis of the unit cell normal to the film surface on the substrate. The (003) diffraction peak at $2\theta = 18.5^\circ$ in the XRD of the $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ film corresponds to an interplanar spacing of 0.145 nm. These results suggest that the layered structure grows with an interlayer spacing of 0.145 nm.

It is well-known that the degree of crystallinity is characterized by two important factors: (1) the intensity and (2) the full width at half-maximum (fwhm) of the (003) peak.¹⁸ Variation in (003) peak intensity with deposition temperature is shown in Figure 2a. The scanning electron microscopy (SEM) image of $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ films grown at 450 °C is shown in Figure 2b. It is evident from Figure 2a that the intensity of the (003) peak increases with the increase in growth temperature, which indicates an increase in the grain size. The SEM image provides the evidence for the crystallinity and morphology of the films grown at higher temperatures. The significant increase in intensity, associated with an increase in grain size, as a result of a further increase in T_s beyond 200 °C can be attributed to the enhanced diffusion rate of impinging laser-produced species on the substrate surface. The grain size (L) is directly related to the surface diffusion similar to

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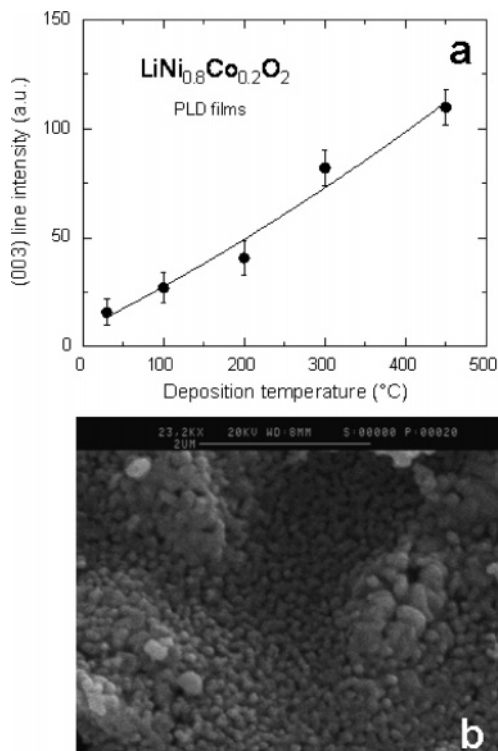


Figure 2. (a) Variation in the (003) peak intensity with deposition temperature for PLD LiNi_{0.8}Co_{0.2}O₂ films. (b) SEM image of LiNi_{0.8}Co_{0.2}O₂ films grown at 450 °C. The crystallinity, increased grain size, and morphology of the films are evident from the image.

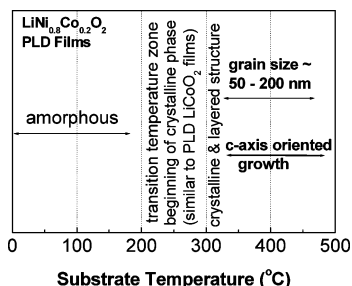


Figure 3. Phase diagram of microstructure development in PLD LiNi_{0.8}Co_{0.2}O₂ films. The microstructure changes in the PLD LiNi_{0.8}Co_{0.2}O₂ films as a function of growth temperature are indicated.

diffusion coefficient which can be expressed as^{20,21}

$$L = L_0 \exp(-Q_d/k_B T_s) \quad (1)$$

where Q_d is the activation energy, k_B is the Boltzmann constant, T_s is the absolute temperature, and L_0 is a pre-exponential factor that depends on the physical properties of the substrate deposit. The activation energy (Q_d) value obtained for the growth of LiNi_{0.8}Co_{0.2}O₂ films is 19 meV. Data are not available in the literature to compare the activation energy of the LiNi_{0.8}Co_{0.2}O₂ film growth by PLD to that of any other method.

On the basis of the experimental results, we propose the phase diagram mapping the effect of growth temperature on the microstructure of PLD LiNi_{0.8}Co_{0.2}O₂ film as shown in Figure 3. It is evident that the temperature, the fundamental thermodynamic parameter, largely governs the growth and

structure of PLD LiNi_{0.8}Co_{0.2}O₂ films. For LiNi_{0.8}Co_{0.2}O₂ films deposited at $T_s < 200$ °C, the impinging flux produced by the laser ablation may be just sticking to the substrate surface at its place of hitting with almost no surface diffusion resulting in an amorphous structure. The adatom mobility increases with increasing growth temperature. The formation of grains and appearance of well-resolved and intense peaks observed in XRD indicates that the growth temperature of 200 °C favors the onset of the crystalline phase. The increased diffusion of adatoms leads to a larger rate of atoms joining together to form grains, the driving force being derived from the tendency of minimizing the surface energy. The onset of crystallization at a lower temperature (200 °C) is perhaps due to the advantage of PLD where the impinging flux has higher kinetic energy when compared to equivalent thermally evaporated and/or sputtered flux. The increase in grain size as a result of further increase in growth temperature beyond 200 °C can be attributed to the enhanced diffusion rate of impinging species on the surface.

Finally, we briefly comment on the structural development and strongly *c*-axis oriented growth of the PLD LiNi_{0.8}Co_{0.2}O₂ films. In general, the important driving forces for the grain-growth are (a) excess free energy in a grain boundary, which makes the grain minimize its local surface area, and (b) the volume free energy difference between the neighboring grains on either side of a grain boundary.²² In crystalline films, the variations in the energies of free surface or the film–substrate interface may provide a driving force for intertransport toward the formation of larger grains.²³ The atomic movement on the substrate surface and arrangement of atoms to (003) orientation as observed in this work suggest that the (003) planes are energetically favorable for PLD LiNi_{0.8}Co_{0.2}O₂ films. Therefore, the preferred orientation of PLD LiNi_{0.8}Co_{0.2}O₂ films is due to the growth mainly occurring along *c* axis to minimize the internal strain energy. This is due to the fact that in the crystalline materials anisotropy exists, the strain energy densities will typically be different for different crystallographic variations, and the grain growth will favor those orientations with low strain energy density.²⁴

Because the impetus for the work is to use the grown PLD LiNi_{0.8}Co_{0.2}O₂ films in microbattery application, we show the typical electrochemical charge–discharge curves of Li//LiNi_{0.8}Co_{0.2}O₂ cells in Figure 4. Electrochemical measurements, for a representative PLD LiNi_{0.8}Co_{0.2}O₂ film shown in Figure 4, were carried out at a rate *C*/30 in the potential range 2.5–4.2 V. As such, the voltage profile should provide a close approximation to the open-circuit voltage (OCV). Electrochemical measurements were carried out on Li//LiNi_{0.8}Co_{0.2}O₂ cells with a lithium metal foil as the negative electrode and a LiNi_{0.8}Co_{0.2}O₂ film as the positive electrode of 1.5 cm² active area using a Teflon homemade cell hardware. The Ni substrate was covered by insulating epoxy leaving only the PLD film as the active area. The electrolyte consisted of 1 M LiClO₄ dissolved in propylene carbonate.

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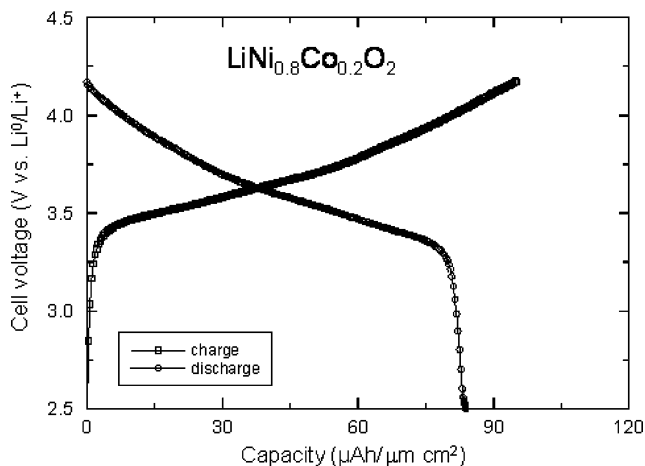


Figure 4. Initial charge–discharge capacity curves for the PLD $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ film.

Electrochemical titration was made by charging and discharging the cells using the galvanostatic mode of a MacPile system in the potential range between 2.5 and 4.3 V. Quasi-OCV profiles were recorded using current pulses of $4 \mu\text{A}/\text{cm}^2$ supplied for 1 h followed by a relaxation period of 0.5 h. The general remarks derived from the charge–discharge curves are as follows:

(i) An initial voltage of about 2.6 V versus Li^0/Li^+ is measured for PLD $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ film electrodes, which is close to that recorded on the galvanic cell using crystalline material.²⁵

(ii) The cell-voltage profiles display the typical profile currently observed for $\text{Li}_x\text{Ni}_{1-y}\text{Co}_y\text{O}_2$ materials.²⁶

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(iii) The cell voltage is a function of the structural arrangement in the film and thus depends strongly on the substrate temperature.

However, it was found that the potential values measured are slightly increased for films grown at higher growth temperature.

In summary, $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ films have been fabricated by PLD. The effect of several variables such as growth temperature, oxygen partial pressure, and target composition on the growth mode, structure, and phase stability is investigated. Structural characterization using XRD provided evidence for the excellent structural quality and phase stability of the grown PLD $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ films. A combination of the process parameters, the target composition (lithium-rich), the growth temperature, and the oxygen partial pressure promotes construction of a stoichiometric single phase with the layered structure in the films. The activation energy of the $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ film growth is 19 meV. The phase diagram for the microstructure development in PLD $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ films is proposed, which could provide a road map to optimize the deposition process parameters to grow films with controlled structure for the desired technological applications. The applicability of the grown PLD $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ films in microbattery devices is demonstrated. A more detailed account of the surface chemistry, structure–property relationship, and electrochemical device performance of PLD $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ films is forthcoming. It is important to recognize that the improved understanding of the structure–growth condition(s) relationship along with the demonstration of applicability of the grown PLD $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ films in device applications as presented in this communication will significantly contribute to the science and technology.

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