

Growth of layered $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$ thin films by pulsed laser deposition for application in microbatteries

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$\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$ films were prepared by pulsed laser deposition on stainless steel (SS) and Au substrates. The substrate was found to play an important role in determining the growth of films. Although similar x-ray diffraction spectra were observed for both types of substrates, Raman spectra exhibited different features. The charge-discharge behavior of the film on the SS substrate indicates a spinel structure while the charge-discharge behavior of the film on the Au substrate indicates a layered structure. The secondary ion mass spectrometry depth-profiling results indicate interdiffusion between the film and the substrate, which inhibits the formation of pure layered $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$ phase. © 2008 American Institute of Physics. [DOI: 10.1063/1.2829605]

There is a growing interest in developing thin film microbatteries as power sources for the ever increasing micro- and nanodevices such as nanoelectromechanical systems, smart cards, implantable medical devices, and microsensors.^{1,2} To realize thin film microbatteries for various applications, the development of a high-quality cathode film with high energy density, good reversibility, stable working voltage, and low cost is imperative. Lithium transition metal oxides are widely used as cathode materials for lithium-ion batteries due to their high working voltage, large theoretical capacity, fast lithium diffusion channels, and good structural stability.^{3,4} Therefore, recent interest in the development of solid-state lithium microbatteries has generated extensive research on fabrication and characterization of lithium transition metal oxide films in view of their potential application as a cathode film for microbatteries.^{5–8}

Layered lithium transition metal oxides, of the general formula LiMO_2 ($M = \text{Co}, \text{Ni}, \text{or Mn}$) have attracted considerable interest as cathode materials for lithium-ion batteries.^{3,4} Among them, LiCoO_2 is a typical example and has been widely used in the commercial batteries. However, people are searching for alternative cathode materials to replace LiCoO_2 due to its high cost, toxicity, limited capacity, and structural instability at high voltage.⁹ Recently, layered $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$ has been extensively studied as a promising cathode material with low cost, nontoxicity, large theoretical capacity, and good structural stability.^{9,10} Therefore, we are encouraged to attempt the synthesis of $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$ thin films for developing next-generation microbatteries. In this letter, we report the synthesis and characterization of $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$ thin films on two types of substrates grown by pulsed laser deposition (PLD). The substrate was found to play an important role in determining the composition and microstructure of $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$ thin films.

$\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$ thin films were grown on stainless steel (SS) and Au substrates by PLD in a vacuum chamber at a base pressure less than 10^{-5} Torr. SS is normally used as

substrate to grow thin film electrodes due to its stability against the liquid electrolyte and low cost. However it may not be suitable for some of thin films especially for those which need high temperature processing. Therefore, Au substrate was also selected in this study due to its high chemical stability at high temperature. The target was prepared by sintering a mixture of LiOH (99%, Alfa Aesar), NiO (99%, Alfa Aesar), and MnO_2 (99.9%, Alfa Aesar) at 1000 °C in air for 12 h. To compensate the lithium loss during the deposition, excess LiOH was added leading to a $\text{Li}/(\text{Ni}+\text{Mn})$ ratio of 1.5 in the mixture. A Lambda Physik KrF excimer laser with wavelength 248 nm was used in the deposition. The laser fluence and repetition rate were controlled at 2 J cm^{-2} and 10 Hz, respectively. The thin films were deposited at a substrate temperature of 550 °C with an oxygen partial pressure of 2 Torr. Postannealing of thin films was conducted in the furnace with an oxygen flow at a temperature from 650 to 950 °C for 3 h. The thickness of thin films is about 300–500 nm characterized by field emission scanning electron microscopy. The structure and crystallinity of the films were investigated using a Shimadzu XRD-6000 x-ray diffractometer with $\text{Cu K}\alpha$ radiation and a Jobin-Yvon T6400 micro-Raman system equipped with a charge-coupled device detector. Raman spectra were recorded using the 514.5 nm line of an Ar^+ laser at a power level of 5 mW. Electrochemical measurements were carried out using a Solartron 1287 cell test system. The Swagelok type cells consist of a Li-metal foil counter electrode, a $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$ thin film working electrode, and 1 M LiPF_6 in ethyl carbonate/dimethyl carbonate solution (1/1 vol %) as the electrolyte. Galvanostatic charge-discharge measurements were carried out in the voltage range of 2.5–4.5 V with a constant current density of $2 \mu\text{A}/\text{cm}^2$. The secondary ion mass spectroscopy (SIMS) depth profiles of thin film samples were carried out by a Cameca IMS 6f using 12.5 keV O_2^+ as a primary ion source.

Figure 1(a) shows the x-ray diffraction (XRD) spectra of the $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$ thin films deposited on SS substrates at different annealing temperatures from 650 to 850 °C. The

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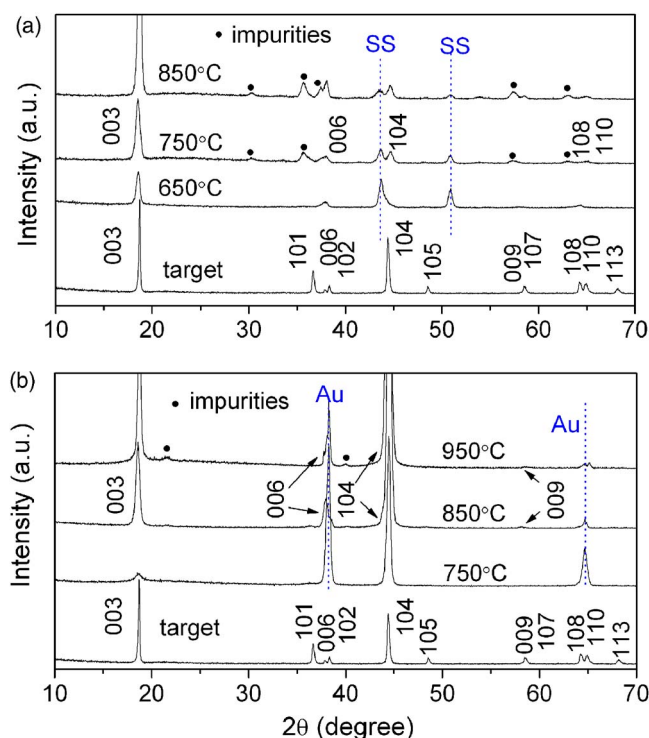


FIG. 1. (Color online) (a) XRD spectra of the $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$ thin films deposited on the SS substrates at different annealing temperatures and (b) XRD spectra of the $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$ thin films deposited on the Au substrates at different annealing temperatures.

XRD spectrum of the target is also shown at the bottom of the figure to help index the diffraction peaks of thin films. It can be seen that a (003) texture of the film develops as the annealing temperature increases from 650 to 850 °C. The film annealed at 650 °C seems to be in a single phase without indication from impurities. However, as the annealing temperature increases, impurity peaks start to emerge and become very pronounced at 850 °C. The impurity peaks formed above 650 °C can be attributed to nickel oxide (NiO), manganese oxide (Mn_2O_3 and MnO_2), and iron oxide (Fe_2O_3). The formation of impurities of nickel oxide and manganese oxide is probably due to the lithium loss at high annealing temperatures. The possible impurity of iron oxide suggests that iron diffusion into the film from the substrate at high annealing temperatures. Figure 1(b) shows the XRD spectra of the $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$ thin films deposited on the Au substrates at different annealing temperatures from 750 to 950 °C. Similar to the thin films grown on the SS substrates, thin films grown on the Au substrates also develop a (003) texture as the annealing temperature increases. The thin films grown on the Au substrates only exhibit two very small impurity peaks at a very high annealing temperature of 950 °C. The two impurity peaks can be attributed to Li_2MnO_3 and Mn_2O_3 . Besides layered structure, spinel structure has been identified in this material when synthesized at very low temperature.¹¹ Since XRD patterns of spinel and layered structures are quite similar to each other with only small difference, from the limited diffraction peaks of the thin film XRD spectrum, it is difficult to determine whether or not there exists a layered structure.

To further investigate the structure of the films, Raman scattering (RS) measurements were carried out on the two types of thin films. Figure 2 shows the RS spectra of the

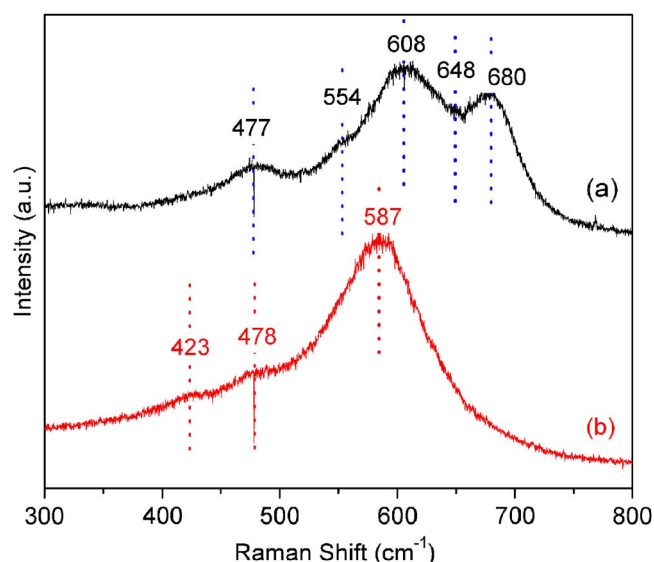


FIG. 2. (Color online) Raman scattering spectra of (a) the $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$ thin film grown on the SS substrate (650 °C) and (b) the $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$ thin film grown on the Au substrate (750 °C).

$\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$ thin film grown on the SS substrate (annealed at 650 °C), and the $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$ thin film grown on the Au substrate (annealed at 750 °C). The material with layered structure normally displays two Raman-active modes, A_{1g} and E_g , as predicted by the theoretical factor-group analysis of the $R3-m$ rocksalt structure.¹² As shown in Fig. 2(b), the Raman spectrum of the $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$ thin film grown on the Au substrate exhibits three Raman bands peaked at 423, 478, and 587 cm^{-1} . The RS bands at 478 and 587 cm^{-1} match well with Raman-active E_g and A_{1g} modes reported for layered $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ (Ref. 13) and $\text{Li}_{1.07}\text{Ni}_{10.1}\text{Co}_{0.6}\text{Mn}_{0.23}\text{O}_2$,¹⁴ while the very small band observed at 423 cm^{-1} is probably related to Li_2MnO_3 super lattice ordering, as reported by Jeong *et al.*¹⁴ However, the RS spectrum of the film grown on the SS substrate exhibits very different spectral features. As shown in Fig. 2(a), a series of broadbands located at 477, 554, 590, 620, and 685 cm^{-1} can be observed. The appearance of three high-wave-number bands above 600 cm^{-1} , which are often observed from the RS spectrum of spinel phase,¹⁵ probably implies the existence of spinel phase in the film.

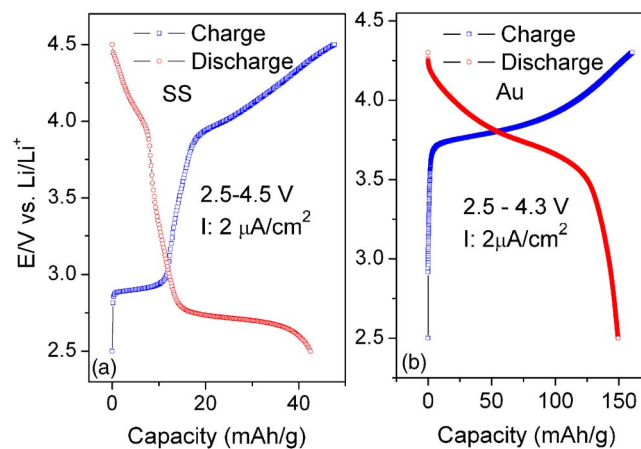


FIG. 3. (Color online) Typical charge-discharge curves of (a) the $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$ thin film grown on the SS substrate (650 °C) and (b) the $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$ thin film grown on the Au substrate (750 °C).

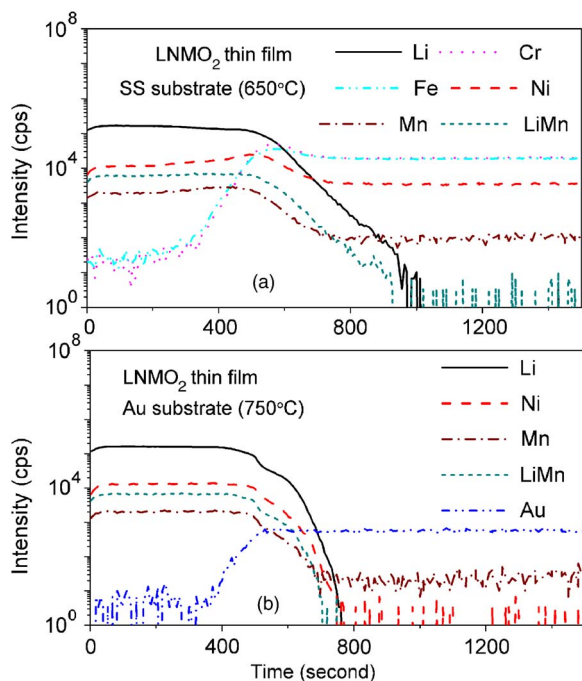


FIG. 4. (Color online) SIMS depth profiles of (a) the $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$ thin film grown on the SS substrate (650°C) and (b) the $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$ thin film grown on the Au substrate (750°C).

Galvanostatic charge-discharge measurements were performed on the $\text{Li}/\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$ cells assembled using two types of thin film samples. Figure 3(a) shows the typical charge-discharge curve of the $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$ film grown on the SS substrate in the voltage range between 2.5 and 4.5 V at a constant current density of $2\ \mu\text{A}/\text{cm}^2$. A voltage plateau between 2.5 and 3 V can be clearly seen from both charge and discharge. The voltage plateau between 2.5 and 3 V is typical charge-discharge behavior of spinels such as LiMn_2O_4 and $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$.^{16,17} In addition, the overall reversible capacity for the film between 2.5 and 4.5 V is only about 40 mAh/g, which is much less than the capacity can be delivered in this voltage range for $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$ composite electrode.¹¹ This observation clearly indicates that the film does not have a pure layered structure but consist of some spinel phase, which is consistent with the conclusion obtained from the Raman measurement. Figure 3(b) shows the typical charge-discharge curves of the $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$ thin film grown on the Au substrate in the voltage range between 2.5 and 4.3 V at a constant current density of $2\ \mu\text{A}/\text{cm}^2$. Upon charge, the cell voltage steeply increases to about 3.75 V and then slowly increases to 4.3 V. Similar behavior can be observed for the discharge process. The charge-discharge behavior and the reversible capacity ($\sim 150\ \text{mAh}/\text{g}$ between 2.5 and 4.3 V) of the film grown on the Au substrate are in good agreement with those of composite electrodes.¹¹ The absence of voltage plateaus between 2.5 and 3 V indicates that the film grown on the Au substrate has a pure layered phase.

The above results indicate that the $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$ thin film grown on the Au substrate exist in a pure layered phase while the film grown on the SS substrate develop some spinel phase. It is speculated that the structural difference in the two types of films is probably due to the different substrate materials, which may induce different reaction or interdiffu-

sion between thin film and substrate during the high temperature annealing process. To investigate the interdiffusion between the film and the substrate, SIMS measurements were performed on the two types of thin films. Figure 4(a) shows the SIMS depth profile of the $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$ thin film grown on the SS substrate (annealed at 650°C). The region where the ion counts profiles of Li, Ni, and Mn from the film lower while ion counts profiles of Fe and Cr from the substrate rise indicates the interface region between the film and the substrate. It is clear that all ion counts profiles develop a gentle slope at the interface region, which suggests severe interdiffusion between the film and the SS substrate. It can be seen that Li diffusion into the substrate is especially pronounced. The severe interdiffusion between the film and substrate may probably change the thin film composition, inducing some spinel phase and prohibit the formation of layered phase. Figure 4(b) shows the SIMS depth profile of the $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$ thin film grown on the Au substrate (annealed at 750°C). Although the film grown on the Au substrate was annealed at a higher temperature, all ion counts profiles develop a very steep slope at the interface region, indicating no distinct interdiffusion between the film and the Au substrate.

In summary, the $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$ thin films with a pure layered phase have been prepared on the Au substrates by PLD. Substrate plays an important role in growing layered $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$ thin films. The film grown on the SS substrate cannot develop a pure layered phase due to the severe interdiffusion between the substrate and the film during the high temperature annealing process while the Au substrate has been proved to have limited interdiffusion with the film. The electrochemical behavior of the $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$ thin film grown on the Au substrate agrees well with literature report on the composite electrode, which makes it promising for application in microbatteries.

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