OPTOELECTRONICS AND ADVANCED MATERIALS – RAPID COMMUNICATIONS Vol. 6, No. 3-4, March - April 2012, p. 508 - 510

Substrate effect on microstructure of $LiCoO_2$ thin film cathodes

M. C. RAO*, SK. MUNTAZ BEGUM
Department of Physics, Andhra Loyola College, Vijayawada – 520008, India

---

$LiCoO_2$ thin films were prepared by pulsed laser deposition technique on different substrates with respect to deposition parameters. The surface morphological features of the deposited films were studied by scanning electron microscopy (SEM) with respect to different substrates. The SEM data demonstrated that the $LiCoO_2$ films deposited on Pyrex glass substrate have rough surface with several dispatches of grains, where as the films deposited on silicon substrate showed very fine and uniform particles without dispatches of grains. The films deposited on flexible substrate showed non-uniform grains and dispatches of grains due to discontinuity in the film. These results showed that the selection of an appropriate substrate is important for fabricating the thin film electrode with the high rate capacity, especially considering the application of microbatteries.

(Received February 28, 2012; accepted April 11, 2012)

Keywords: $LiCoO_2$, Thin films, PLD, Pyrex glass, flexible, Silicon substrates

---

1. Introduction

Recently, thin films of functional materials including oxide ceramics have become important for use in many electronic, photonic, magnetic, ionic, etc., devices. Most of them have been fabricated through the so-called highly technical processing routes that require a high consumption of energy (such as physical vapor deposition [1], chemical vapor deposition [2], dip coating with firing [3]). However, we must consider also total environmental load of these processing in addition to their capability. There is a growing interest in thin film batteries with smaller dimension. The cathode is one of the critical components of a lithium-ion battery and it determines the capacity, cyclic performance and thermal stability of the battery. In order to improve the electrochemical properties of the cathode material, researchers have attempted to modify the cathode surface by using stable materials [4]. The layered transition metal oxide compounds which are composed of hexagonal close packed oxygen atoms network with lithium and transition metal ions in an alternating (111) planes, such as $LiCoO_2$, $LiNiO_2$, $LiCo_xNi_{1-x}O_2$ etc. have been studied extensively as alternate cathode materials for low power applications. 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.

$LiCoO_2$ is the most commonly used cathode material for rechargeable Li-ion batteries. Without the presence of a polymer binder and carbonaceous powders, the dense and flat thin films are ideally suited to study fundamental kinetic parameters such as lithium diffusivity. The layered structure of $LiCoO_2$, a nearly cubic close-packed arrangement of oxygen ions with lithium and cobalt ions occupying alternate layers of octahedral sites, is well suitable for the rapid deintercalation and intercalation of lithium. When lithium is deintercalated or intercalated from or into the Li_xCoO_2 matrix, transformations of several phases occur as the lithium content, x, is varied between $x = 1$ and 0.5. These include a metal–insulator transition and order–disorder reactions. Lithium diffusion in the electrodes is a key factor that determines the rate at which a battery can be charged and discharged. With increasing interest in high power density, the kinetics of Li diffusion becomes more important.

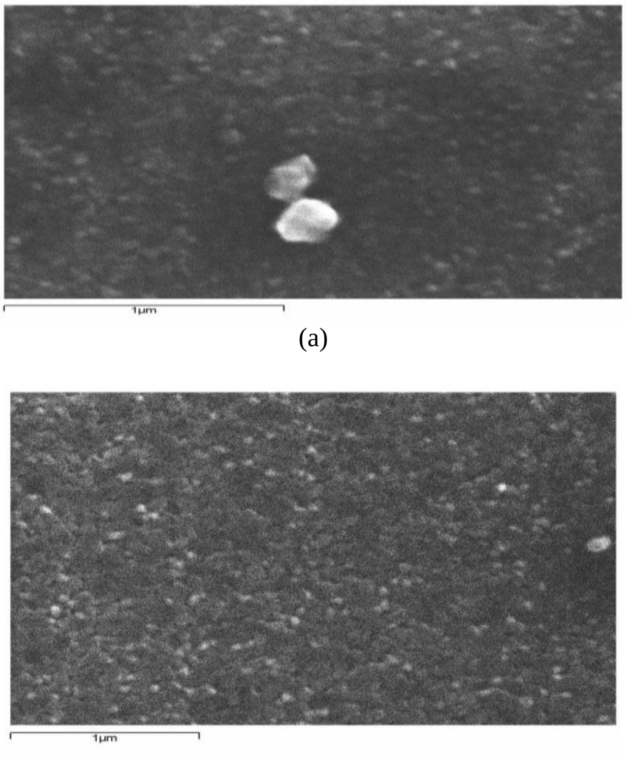
The growth of $LiCoO_2$ thin films with preferred orientation is known to be crucial. Several thin film deposition techniques such as pulsed laser deposition [5-11], electrostatic spray deposition [12] and chemical vapour deposition [13] were employed for the growth of $LiCoO_2$ thin films. PLD has been widely recognized as a very promising, versatile and efficient method for the deposition of metal oxide thin films [14]. PLD is a powerful and flexible technique for fabricating simple and complex metal oxide films, and has several advantages for thin film deposition: (1). Direct stoichiometry transfer from the target to the growing film. (2). High deposition rate and inherent simplicity for the growth of multilayered structures. (3). Dense, textured films can be produced more easily by PLD with in situ substrate heating. 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. Iriyama et al. [9] prepared thin films of $LiCoO_2$ by PLD and studied the electrochemical performance. In thin film deposition, the substrate plays the important role of determining the microstructure and surface morphology of films deposited on it. Because these two parameters, i.e., the microstructure and morphology, affect the electrochemical properties of lithium intercalation electrodes, choosing an appropriate substrate for the deposition of electrode materials is critical for developing a thin film electrode for lithium microbatteries. In this study, we have deposited $LiCoO_2$ thin films on different substrates, i.e., Pyrex glass, flexible and silicon substrates and investigated substrate effects on the microstructural properties of thin film cathodes. The surface morphologies of the films on each substrate were very different from each other.

2. Experimental

$LiCoO_2$ films were grown by pulsed laser deposition technique on Pyrex glass, flexible and 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 3 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. 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 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 [15, 16].

3. Results and discussion

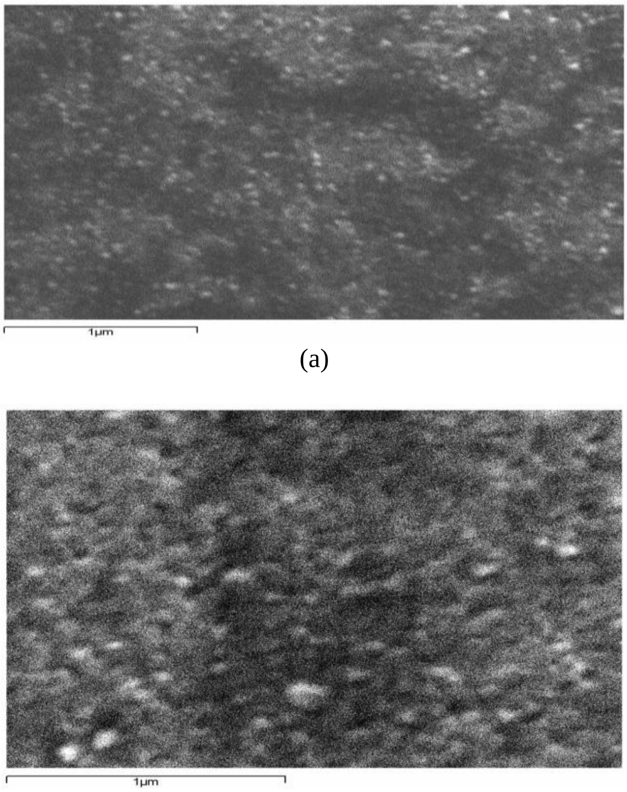
$LiCoO_2$ thin films are deposited by pulsed laser deposition technique on Pyrex glass, flexible and silicon substrates in relation to deposition conditions. The substrate effect on the microstructural properties of these films is systematically studied. Pulsed laser deposited $LiCoO_2$ thin films on Pyrex glass substrate (with low and high magnifications) are shown in Fig. 1. The substrate has rough surface and large particles with several dispatches of grains were observed related to the morphology of Pyrex glass. These dispatches are believed to be caused by thermal stress. The $LiCoO_2$ films deposited on flexible substrates (with low and high magnifications) showed (Fig. 2) a flat and uniform surface morphology at higher oxygen partial pressures, whereas at lower oxygen partial pressures, non-uniform grains and dispatches of grains are observed because of discontinuity in the film is observed due to deficiency of lithium or oxygen or both in $LiCoO_2$ thin films.



(a)

(b)

Fig. 1. $LiCoO_2$ films deposited on Pyrex glass substrate (a) low magnification (b) high Magnification.

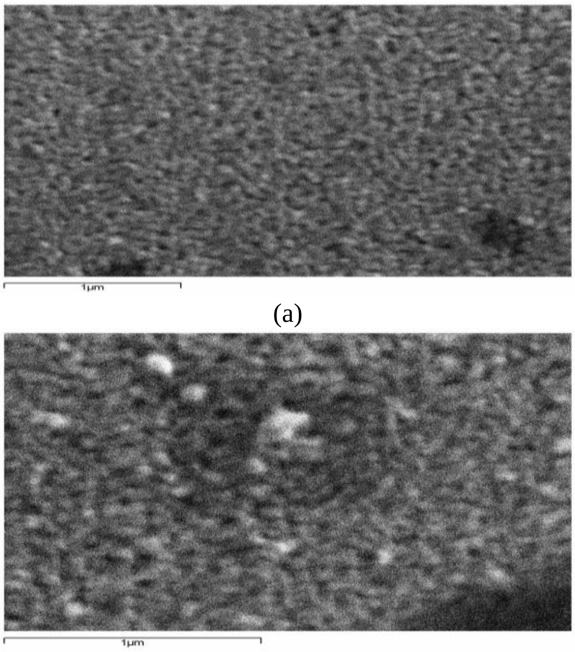


(a)

(b)

Fig. 2. $LiCoO_2$ films deposited on flexible substrate (a) low magnification (b) high Magnification.

Pulsed laser deposited $LiCoO_2$ thin films on silicon substrates (with low and high magnifications) are shown in Fig. 3. These films are pin-hole free as revealed from optical microscopy and well adherent to the substrate surface. The films consisting of very fine and uniform particles without dispatches of grains were observed at lower temperature. The effect of substrate temperature allows causing the motion of small islands, which then coalesced with larger grains. The mobility of the island on the substrates and number of islands with sufficient energy to move are determined by a thermal activated process. Thus the film deposited at higher substrate temperature has a higher coalescence speed and that speed gradually increases in the films, the islands combine, nucleation occurs and coalesced with each other to form continuous film with larger grain size. It was reported that high the substrate temperature, the less porous the layer. Therefore, the reaction between $LiCoO_2$ and Li_2O contributes to the formation of this dense morphology. These results are in consistent with the data reported earlier [17, 18]. Surface morphology is interesting and useful to provide better understanding of the electrode characteristics of a rechargeable lithium microbattery. From these results, it should be recognized that the selection of an appropriate substrate is important for fabricating the thin film electrode with the high rate capacity, especially considering the application of microbatteries to devices requiring a high pulse current such as a microsensor or a hazard card [19].



(a)

(b)

Fig. 3. $LiCoO_2$ films deposited on silicon substrate (a) low magnification (b) high Magnification.

4. Conclusion

We have studied the substrate effect on the microstructural properties of thin film $LiCoO_2$ electrodes. The SEM data demonstrated that the $LiCoO_2$ films deposited on Pyrex glass substrates have rough surface with several dispatches of grains, where as the films deposited on silicon substrate showed very fine and uniform particles without dispatches of grains. The films deposited on flexible substrates showed non-uniform grains and dispatches of grains due to discontinuity in the film. Therefore, it was concluded that the choice of an appropriate substrate is very important for fabricating a thin film electrode with high rate capacity, especially considering the application of microbatteries to devices requiring a high pulse current such as a microsensor or a hazard card.

Acknowledgements

The Corresponding author (M. C. Rao) is thankful to UGC for providing the financial assistance through Major Research Project (Link No. F.No. 40-24/2011(SR)).

References

[1] M. Ohring, in: The Materials Science of Thin Films, Academic Press, San Diego, CA, 79 (1992).
[2] M. Ohring, in: The Materials Science of Thin Films, Academic Press, San Diego, CA, 147 (1992).
[3] S. Komarnei, S. Sakka, P. P. Phule, R. M. Laine, in: _Sol–Gel Synthesis and Processing, Ceramic Transactions, The American Ceramic Society, Westerville, OH, USA, **95 (**1998).
[4] H. J. Lee, K. S. Park, Y. J. Park, J. Power Sources **195,** 6122 (2010).
[5] P. J. Bouwman, B. A. Boukamp, H. J. M. Bouwmeester, P. H. L. Notten, Solid State Ionics **152**, 181 (2002).
[6] C. L. Liao, K. Z. Fung, J. Power Sources **128**, 263 (2004).
[7] C. L. Liao, Y. H. Lee, K.. Z. Fung, J. Alloys Compd. **436**, 303 (2007).
[8] C. S. Nimisha, M. Ganapathi, N. Munichandraiah, G. Mohan Rao, Vacuum **83**, 1001 (2009).
[9] Y. Iriyama, T. Inabu, A. Abe, Z. Ogumi, J. Power Sources **94**, 175 (2001).
[10] H. Xia, L. Lu, G. Ceder, J. Power Sources **159**, 1422 (2006).
[11] S. B. Tang, M. O. Lai, L. Lu, J. Alloys Compd. **449**, 300 (2008).
[12] C. H. Chen, A. A. J. Buysman, E. M. Kelder, J. Schoonman, Solid State Ionics **80**, 1 (1995).
[13] G. Chai, S. G. Yoon, J. Power Sources **125**, 236 (2004).
[14] J. C. Miller, R. F. Haglmel, JR., Laser Ablation and Deposition, Academic Press, New York (1998).
[15] M. C. Rao, J. Crys. Growth **312**, 2799 (2010).
[16] M. C. Rao, Optoelect. Adv. Mater., - Rapid Commun. **5**(1), 85 (2011).
[17] K. A. Striebel, C. Z. Deng, S. J. Wen, E. J. Cairns, J. Electrochem. Soc. **143,** 1821 (1996).
[18] F. K. Shokoohi, J. M. Tarascon, B. J. Wilkens, D. Guyomard, C. C. Chang, J. Electrochem. Soc. **139,** 1845 (1992).
[19] J. K. Lee, S. J. Lee, H. K. Baik, H. Y. Lee, S. W. Jang, S. M. Lee, Electrochem. Solid State Lett., **2**, 512 (1999).

---

[*] Corresponding author: raomc72@gmail.com