JOURNAL OF OPTOELECTRONICS AND ADVANCED MATERIALS Vol. 13, No. 4, April 2011, p. 428 - 431

Grain size effect on the growth of $LiCoO_2$ thin film cathodes

M. C. RAO
Reader in Physics, Andhra Loyola College, Vijayawada – 520 008, Andhra Pradesh, India

Thin films of $LiCoO_2$ were grown by pulsed laser deposition technique on silicon substrates. Microstructural properties were studied with respect to their deposition parameters i.e. substrate temperature (T_s), oxygen partial pressure (pO_2) and target composition in the deposition chamber. The atomic force microscopy (AFM) data demonstrated that the pulsed laser deposited $LiCoO_2$ thin films are homogeneous and uniform with regard to the surface topography. For the film deposited at 300 ^{0}C in oxygen partial pressure of 100 mTorr (prepared from target with 15% Li_2O) is composed of roughly spherical grains of varying sizes and the average grain size is estimated. The root mean square surface roughness of the films derived from AFM data is 8 nm. The grain size increased with the increase of substrate temperature. The increase in grain size with deposition temperature is clearly observed in AFM data and found to be around 210 nm for the films deposited at 700 ^{0}C. The surface morphological features of pulsed laser deposited films grown at various substrate temperatures were also studied by scanning electron microscopy and the results are compared with AFM data.

(Received January 10, 2011; accepted April 11, 2011)

Keywords: $LiCoO_2$ thin films, PLD, AFM, SEM

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. The trend of power sources, in accordance with the shrinkage in the size of electronic devices, shifted from city line to regular batteries, and final goal may be miniature power sources. A strictly solid state battery would be a microbattery operating as a solid state device where the positive charge is transported by small ions diffusing through a perfect electronic insulator and the negative charges are transported by electrons injected from the external circuit. Lithiated transition metal oxides such as $LiMO_2$ (Where M = Co, Ni, Mn etc.) have received considerable attention in recent years as high voltage positive electrode materials for use in secondary lithium batteries [1]. Among these, the high cycling stability and high cell potential against lithium makes $LiCoO_2$ an attractive cathode material in the fabrication of all solid state rechargeable microbatteries [2, 3].

$LiCoO_2$ crystallizes in the layered rock-salt α-$NaFeO_2$ type structure with hexagonal lattice parameters a = 2.815 Å and c = 14.049 Å. The rock salt $LiCoO_2$ lattice consists of a close packed network of oxygen ions with lithium and cobalt ions on alternating (111) planes of the cubic rock salt sublattice. The Co and Li cations occupy the octahedral 3a and 3b sites, respectively, while oxygen anions are located on the 6c sites, The CoO_6 octahedra are shared edges to form CoO_2 sheets and Li ions can move in two dimensional (2-D) directions between the CoO_2 slabs. Thus the layered $LiCoO_2$ has an anisotropic structure and thereby 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 [2, 4], pulsed laser deposition [4-8], electrostatic spray deposition [9] and chemical vapour deposition [10] were employed for the growth of $LiCoO_2$ thin films. A brief literature survey reveals that it is difficult to grow stoichometric and stable c - axis oriented $LiCoO_2$ thin films by several physical vapour deposition methods due to many growth kinetic processes which occur in vacuum or at low oxygen partial pressures.

Pulsed laser deposition (PLD) has been widely recognized as a very promising, versatile and efficient method for the deposition of metal oxide thin films [11]. 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. This technique is an ideal to grow thin films of exotic materials when only a small quantity is available. 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 turnaround time when growing a thin film of a new material starting from its powder form. Preliminary investigations on pulsed laser deposited $LiCoO_2$ thin films were carried out by Julien et al. [5]. Iriyama et al. [6] and studied the electrochemical performance. They observed that the reactivity in single-phase region at potentials more positive than 4.0 V was lower than that of randomly oriented films. Poly-crystalline layered $R\overline{3}m$ phase thin films of $LiCoO_2$ were grown by PLD using Nd:YAG laser by Julien et al. [12]. In the present study the influence of deposition parameters on the morphological studies 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. 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 [13]. The surface topography was investigated by atomic force microscopy (AFM) using a bench apparatus (Digital instruments, 3100 series). The surface morphology was also studied by JEOL 2000.

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 thickness of $LiCoO_2$ films is 250 nm. The influence of oxygen partial pressure and deposition temperature on the surface morphology of the films is systematically studied. The chemical compositional studies made on $LiCoO_2$ films revealed that a minimum of 100 mTorr oxygen partial pressure is required to grow nearly stoichiometric films.

3.1 AFM studies

The atomic force microscopy data demonstrated that the pulsed laser deposited $LiCoO_2$ thin films are homogeneous and uniform with regard to the surface topography and thickness over an area of 1 cm^2. The surface topography of $LiCoO_2$ film deposited for pure target on silicon substrates recorded by atomic force microscopy at $T_s = 300\ ^0C$ in $pO_2 = 100$ mTorr observed to be composed of irregular grains with high root mean square surface roughness of about 18 nm. The effect of target composition on the film morphology can be understood from the micrographs as long as the layer thicknesses are similar. The AFM picture of $LiCoO_2$ thin film deposited at 300 ^{0}C in an oxygen partial pressure of 100 mTorr prepared from target with 15% Li_2O (Fig. 1) [13] revealed that the film is composed of roughly spherical grains of varying sizes and the average grain size is estimated to be around 80 nm. The root mean square surface roughness of the films derived from AFM data is 8 nm. The individual grains are clearly visible and are seem to be in good contact with each other. The films exhibit characteristic open and porous structure with small grains at lower substrate temperature (300 ^{0}C). In fact this is the advantage of the PLD where nanocrystalline films can be grown at lower substrate temperatures compared to other physical vapour deposition methods. Because of the short distance between the target and the substrate in the PLD technique the films exhibit dense layers with small grains at lower substrate temperatures.

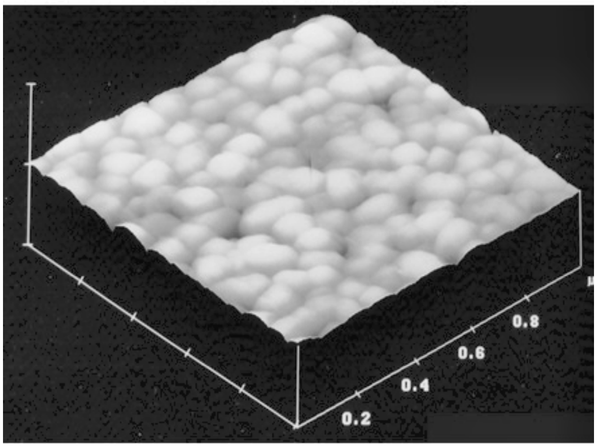


Fig. 1. AFM image of thin film deposited from $LiCoO_2$ target with 15% Li_2O.

The increase in grain size with deposition temperature is clearly observed in AFM data and found to be around 210 nm for the films deposited at 700 ^{0} (Fig. 2) [13] with a root mean square surface roughness of about 15 nm. The surface roughness increases due to the randomness of the grain distribution at higher substrate temperatures. Fig. 3 shows the variation of grain size with the rise in temperature. The morphological changes, grain size enhancement and their distribution characteristics as a result of increase in growth temperature can be explained on the basis of the difference in the mobility of ablated species on the substrate surface as follows. When the laser beam hits the target the ions or molecules or atoms of the target material are liberated. The ablated atomic or molecular or ionic species impinging on the substrate surface (which is at higher temperature) acquire a large thermal energy and hence a large mobility. This enhances the diffusion density of the ablated species. As a result, the collision process initiates the nucleation and enhances the island formation in order to grow a continuous film with larger grains. These results are suitable for the further utilization of PLD films because a fundamental role in terms of charge transfer capability and cycle life is played by the morphology of the films used as cathodes in lithium microbatteries [12].

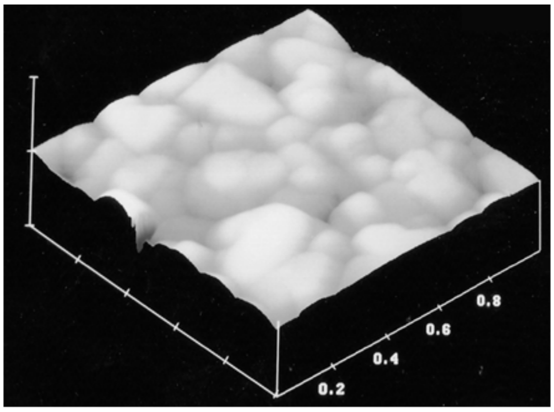


Fig. 2. AFM image of $LiCoO_2$ thin film deposited at substrate temperature of 700 ^{0}C in pO_2 = 100 mTorr.

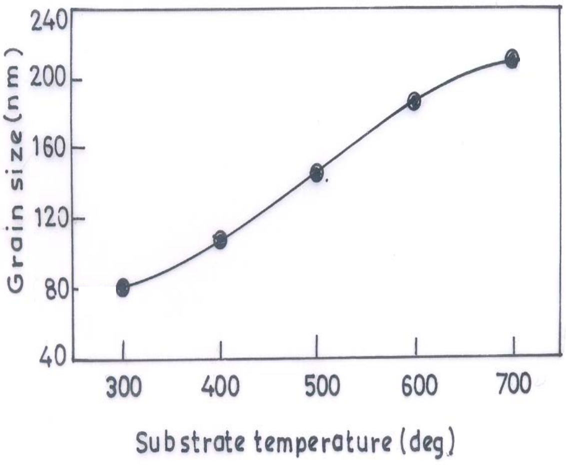
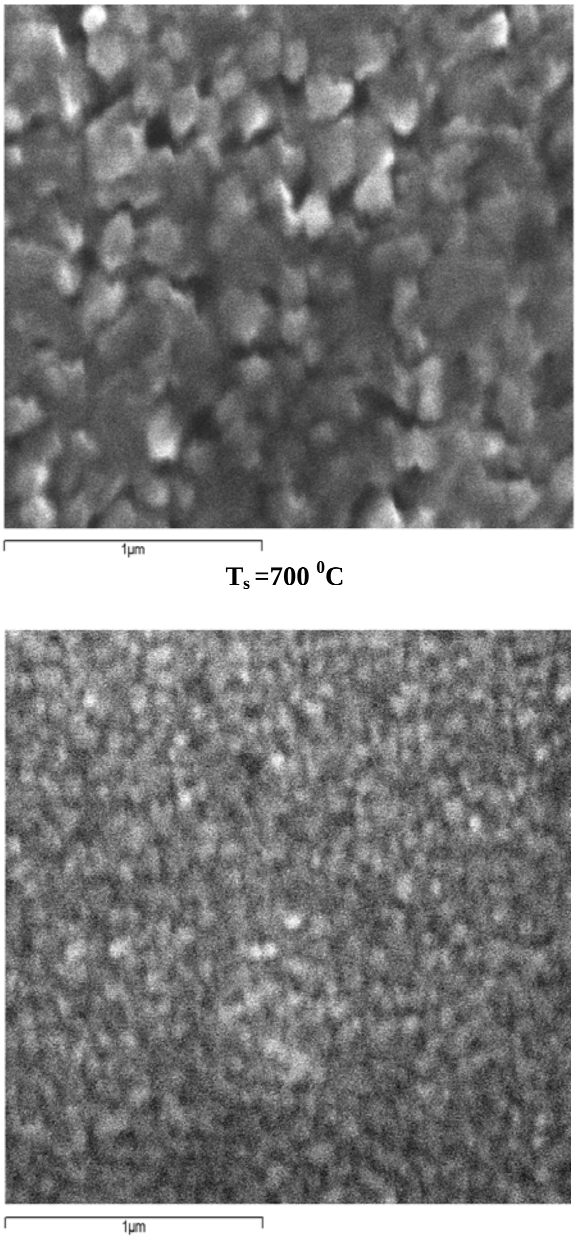


Fig. 3. Variation of grain size of $LiCoO_2$ thin films with substrate temperature.

3.2 SEM studies

The surface morphological features of pulsed laser deposited films grown at various substrate temperatures were also studied by scanning electron microscopy and the results are compared with AFM data.

Scanning electron micrographs of pulsed laser deposited $LiCoO_2$ films grown in oxygen partial pressure pO_2 = 100 mTorr on silicon wafers maintained at 300 ^{0}C and 700 ^{0}C are shown in Fig.4. The SEM micrograph of $LiCoO_2$ thin film grown at 300 ^{0}C exhibits a smooth surface with small roughly spherical grains. For the films deposited at 700 ^{0}C the surface morphology appears to be slightly different. In this case, the film displayed a surface roughness with larger small grains of irregular shape. It was reported that high the substrate temperature, the less porous the layer [14, 15]. Therefore, the reaction between $LiCoO_2$ and Li_2O contributes to the formation of this dense morphology. These results are in consistent with the AFM data.



T_s =700 ^{0}C

T_s =300 ^{0}C

Fig. 4. SEM images of $LiCoO_2$ thin films deposited at different substrate temperatures in pO_2 = 100 mTorr.

4. Conclusions

Thin films of $LiCoO_2$ were prepared by pulsed laser deposition. The atomic force microscopy data demonstrated that the pulsed laser deposited $LiCoO_2$ thin films are homogeneous and uniform with regard to the surface topography. For the film deposited at 300 ^{0}C in oxygen partial pressure of 100 mTorr (prepared from target with 15% Li_2O) is composed of roughly spherical grains of varying sizes and the average grain size is estimated to be around 80 nm. The grain size increased with the increase of substrate temperature and for the film deposited at 700 ^{0}C is 210 nm. SEM results are compared with the AFM data. These results suggest that the open and porous structured $LiCoO_2$ PLD films find potential applications as binder free electrode in the fabrication of all solid state microbatteries.

References

[1] T. Ohzuku, 'Lithium Batteries, New Materials, Developments and perspectives', G. Pistoia, p.239, Elsevier, Amsterdam (1993).

[2] B. J. Neudecker, N.J. Dudney, J.B. Bates, J. Electrochem. Soc. **147**, 517 (2000).

[3] J. B. Bates, N. J. Dudney, B. Neudecker, A. Veda, C. D. Evans, Solid State Ionics **135**, 33 (2000).

[4] P. J. Bouwman, B. A. Boukamp, H. J. M. Bouwmeester, P. H. L.Notten, Solid State Ionics **152,** 181 (2002).

[5] C. Julien, E. Haro-Poniatowski, O. M. Hussain, C. V. Ramana, Ionics **7**, 165 (2001).

[6] Y. Iriyama, T. Inabu, T. Abe, Z. Ogumi, J. Power Sources **94**, 175 (2001).

[7] H. Xia, L. Lu, G. Ceder, J. Power Sources **159**, 1422 (2006).

[8] S. B. Tang, M.O. Lai, L. Lu, J. Alloys & compds. **449**, 300 (2008).

[9] C. H. Chen, A. A. J. Buysman, E. M. Kelder, J. Schoonman, Solid State Ionics **80**, 1 (1995).

[10] W-G. Chai, S-G. Yoon, J. Power Sources **125**, 236 (2004).

[11] J. C. Miller, R. F. Haglmel, JR., 'Laser Ablation and Deposition', Academic Press, New York (1998).

[12] C. Julien, E. Haro-Poniatowski, M. A. Camacho-Lopez, L. Escobar – Alarcon, J. Jimene-Jarquin, Mater. Sci. Eng. B **72,** 36 (2000).

[13] M. C. Rao, J. Crys. Growth **312**, 2799 (2010).

[14] K. A. Striebel, C. Z. Deng, S.J. Wen, E. J. Cairns, J. Electrochem. Soc. **143,** 1821 (1996).

[15] F. K. Shokoohi, J. M. Tarascon, B. J. Wilkens, D. Guyomard, C.C. Chang, J. Electrochem. Soc. **139,** 1845 (1992).

---

*Corresponding author: raomc72@gmail.com