

Growth of LiCoO_2 thin films by Pulsed laser deposition- Measurement of thermodynamic properties

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Lithiated transition metal oxides have received considerable attention in recent years as high voltage positive electrode materials for use in secondary lithium batteries. 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. The synthesis of these compounds in thin film form is of great interest as a result of their possible use as a binder free positive electrode in all solid state microbatteries to power microelectronics. Pulsed laser deposition (PLD) has been widely recognized as a very promising, versatile and efficient method for the deposition of metal oxide thin films. In particular, it has been successfully employed for the deposition of simple and complex metal oxide materials with desired composition, structure, physical and chemical properties. Hence in the present study, thin films of LiCoO_2 were prepared by pulsed laser deposition and the thermo emf of the prepared samples was studied by using thermal probe method. The plot of thermo emf versus temperature difference between the two junctions is found to be linear indicating that the temperature dependence of thermo emf is the characteristic conduction of LiCoO_2 films.

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1. Introduction

Solid state microbatteries now in development may help facilitate three-dimensional high-density integrated circuit technology by providing power to components locally rather than from a remote source, thus reducing “crosstalk” between circuits. An integrable microbattery compatible with the dimensions of microdevices will act as a source of power for many single components in integrated circuits and devices. Advances in science and engineering related to the emerging technologies of lithium-ion batteries (LIBs) have been so spectacular in the past decade that they have become the most popular power source for portable computing, battery cars, microelectronics, biomedical implantable devices and telecommunication[1]. Fabrication of the materials as thin film cathodes for application in all solid state microbatteries has been interesting field of research owing to the miniaturization and the reduced power consumption of many kinds of electronic devices. There is a growing interest in thin film batteries with smaller dimension. The realization of thin film batteries originate from the identification of new thin film cathode materials with high energy density, high specific capacity and structural stability towards lithium insertion. 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 [2, 3].

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. However, we must consider also total environmental load of these processing in addition to their capability. 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 , $\text{LiCo}_x\text{Ni}_{1-x}\text{O}_2$ etc. have been studied extensively as alternate cathode materials for low power applications. Among them, LiCoO_2 has found large scale potential applications in the commercial lithium ion batteries. Although intensive investigations have been devoted in finding most cost effective and less toxic alternate materials like LiMnO_2 , LiMn_2O_4 etc., LiCoO_2 is still so far the most successful, and reliable choice due to superior cycling stability and power density. Also it has been widely used as cathode material due to advantages of high specific capacity, high operating voltage, good reversibility, low self-discharge and long cycle life [4-7].

At present a number of new approaches for the preparation of LiCoO_2 with improved properties have been developed. LiCoO_2 thin films can be obtained by various techniques such as radio frequency (rf) sputtering [7], pulsed laser deposition [8-10], electrostatic spray deposition [11] and chemical vapour deposition [12]. Many efforts have been devoted to investigate the crystal structure and electrochemical properties of LiCoO_2 . Even though the technology is rather expensive and the material is highly toxic, lithium cobaltate is still the most widely used cathode material in lithium-ion batteries. PLD has been widely recognized as a very promising, versatile and efficient method for the deposition of metal oxide thin films [13]. 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. Fig. 1 shows the schematic diagram of the pulsed laser deposition chamber. 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. In thin film deposition, the substrate temperature plays the important role of determining the thermo emf of films. In this study, we have deposited LiCoO₂ thin films on silicon substrates and investigated the thermodynamic properties of these thin films.

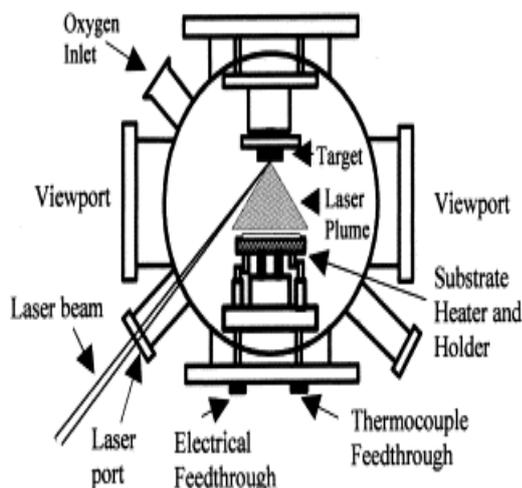


Fig. 1 Schematic diagram of the pulsed laser deposition chamber

2. Experimental

LiCoO₂ films were grown by pulsed laser deposition technique. LiCoO₂ target was prepared by sintering a mixture of high purity LiCoO₂ and Li₂O powders (Cerac products) with excess of Li i.e. Li/Co > 1.0 by adding Li₂O. The mixture was crushed and pressed at 5 tons.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 °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 KrFexcimer 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 mm² 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 [14-16]. The thermo emf of the prepared samples was studied between the temperature ranges from 275 to 325 K by using thermal probe method.

3. Results and discussion

Pulsed laser deposited LiCoO₂ films are pin-hole free as revealed from optical microscopy and well adherent to the substrate surface. The thermo emf of the prepared samples was studied between the temperature ranges from 275 to 325 K.

The thermo power or Seebeck coefficient, of a material measures the magnitude of an induced thermoelectric voltage in response to a temperature difference across that material and the entropy per charge carrier in the material [17]. The term "thermo power" is a misnomer since it does not measure power, but measures the voltage induced in response to a temperature difference. An applied temperature difference causes charged carriers in the material to diffuse from the hot side to the cold side. Mobile charged carriers migrating to the cold side leave behind their oppositely charged nuclei at the hot side thus giving rise to a thermoelectric voltage. Since a separation of charges creates an electric potential, the buildup of charged carriers onto the cold side eventually ceases at some maximum value since the electric field is at equilibrium. An increase in the temperature difference resumes a buildup of charge carriers on the cold side, leading to an increase in the thermoelectric voltage and vice versa. The material's temperature and crystal structure influence S; typically metals have small thermo powers because of half-filled bands caused by equal negative and positive charges cancelling each other's contribution to the induced thermoelectric voltage. In contrast, semiconductors can be doped with excess electrons or electron holes, causing the magnitude of S to be large. The sign of the thermo power determines which charged carriers dominate the electric transport. The temperature difference ΔT between the two ends of a material is small and then the thermo power of a material is defined approximately as:

$$S = - \Delta V / \Delta T$$

and a thermoelectric voltage of ΔV is seen at the terminals.

Fig. 2 shows the schematic representation of Seebeck effect for measuring thermo emf. The thermo emf of laser deposited LiCoO₂ thin film was studied in the temperature range from 275 K - 325 K by using thermal probe method is given in Table-1. The thermo emf was measured and the Seebeck coefficient of the material was also calculated. The plot of thermo emf versus temperature difference between the two junctions is found to be linear (Fig. 3) indicating that the temperature dependence of thermo emf is the characteristic conduction of LiCoO₂ films. The thermo emf of LiCoO₂ films increased with the increasing of temperature. At low temperatures the Seebeck coefficient is observed to be high and the Seebeck coefficient decreases with increasing of temperature. The

large values of thermoelectric power of LiCoO₂ thin films are typical of semiconductor behavior [17].

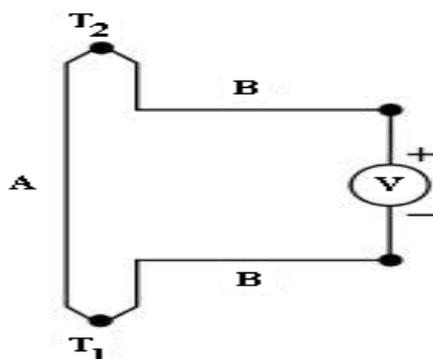


Fig. 2 Schematic representation of Seebeck effect for measuring thermo emf

Table 1 Thermo emf versus temperature

Temperature (K)	Thermo emf (μV)
275	0.412
280	0.752
285	1.095
290	1.354
295	1.692
300	1.932
305	2.254
310	2.613
315	2.916
320	3.224
325	3.615

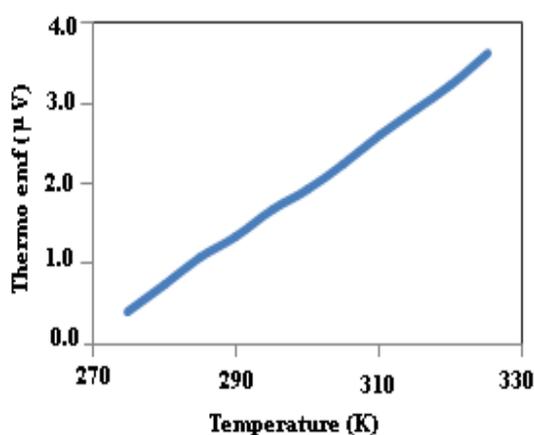


Fig. 3 Temperature dependence of the thermo emf of LiCoO₂ thin film

4. Conclusions

Thin films of LiCoO₂ were grown by pulsed laser deposition technique. The thermo emf of the prepared

samples was studied between the temperature ranges from 275 to 325 K. Pulsed laser deposited LiCoO₂ films are pin-hole free as revealed from optical microscopy and well adherent to the substrate surface. The plot of thermo emf versus temperature difference between the two junctions is found to be linear indicating that the temperature dependence of thermo emf is the characteristic conduction of LiCoO₂ films. At low temperatures the Seebeck coefficient is observed to be high and the Seebeck coefficient decreases with increasing of temperature. The positive value of the Seebeck coefficient revealed that electrons are the majority charge carriers in layered cobalt oxide.

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