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Growth and transport properties of HT–Li_xCoO_2 thin films deposited by pulsed laser deposition

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ABSTRACT

The successful *in situ* growth of single phase, *c*-axis oriented, layered structured Li_xCoO_2 thin films on (0 0 0 1) Al_2O_3 substrates by pulsed laser deposition is reported. Thin films were grown in an oxygen pressure of 1 mbar and substrate temperatures varying from 300 up to 600 °C. It is found that the surface roughness and electrical resistance of the films depends strongly on the deposition temperatures.

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1. Introduction

Li_xCoO_2 has widely been used as a cathode material for lithium ion rechargeable batteries due to its high energy storage capacity and good cycling performance [1]. Thin films of Li_xCoO_2 have attracted a lot of interest due to possible use in micro-batteries for integration in chip and in medical electronics [2].

In the most widespread use as a cathode material, $LiCoO_2$ has a layered rhombohedral structure with space group ($R\bar{3}m$) and lattice parameters of $a_{hex} = b_{hex} = 2.8138$ Å and $c_{hex} = 14.0516$ Å, known as high temperature (HT) phase. It consists of CoO_2 sheets perpendicular to *c*-axis and Li^+ ions form planes between the sheets, allowing free Li^+ ion 2D movement inside the planes. The interesting electrical and thermoelectric properties of this compound can be attributed to the Li^+ ion intercalation/de–intercalation, linked to the redox reactions of the cobalt oxide substructure, which modifies the interaction between the CoO_2 sheets [3,4].

The anisotropic structure of layered Li_xCoO_2 results in transport properties being dependent on the crystallographic orientation of the crystal. In order to fully understand the intrinsic transport mechanism, thin films with preferred growth orientation are desirable. Furthermore the lack of literature reports concerning the growth of smooth, well oriented HT–Li_xCoO_2 films has motivated us to investigate the growth of HT–Li_xCoO_2 thin films using the Pulsed Laser Deposition (PLD) technique.

The PLD technique is highly versatile and has successfully been used for the growth of high quality films for a wide variety of materials with complex stoichiometry and even containing volatile components such as lithiated transition metal oxide thin films [5].

While there are several reports on the growth of $LiCoO_2$ thin films to our knowledge, there is only one recent report [6] addressing the case of HT–$LiCoO_2$ films with smooth surface, which is an important issue in exploiting this material in novel devices. The process reported in [6] for the deposition of smooth epitaxial HT–$LiCoO_2$ films included an *in situ* post-annealing step.

In this paper, we report the PLD growth of HT–Li_xCoO_2 thin films on pristine (0 0 0 1) Al_2O_3 and Cr/Au sputter coated (0 0 0 1) Al_2O_3 substrates in a single step process, *i.e.*, without post–annealing, and discuss their structural, morphological and electrical properties.

2. Material and methods

2.1. Ceramic target preparation

Fine crystalline Li_xCoO_2 powders were prepared by solid-state reaction of slightly non-stoichiometric amounts of Li_2CO_3 (99%) and Co_3O_4 (99.7%). A small excess (3–5 wt%) of Li_2CO_3 is added in the initial step to compensate for the slight volatilisation of lithium oxide during the reaction. Weighing is carried out in a glove box

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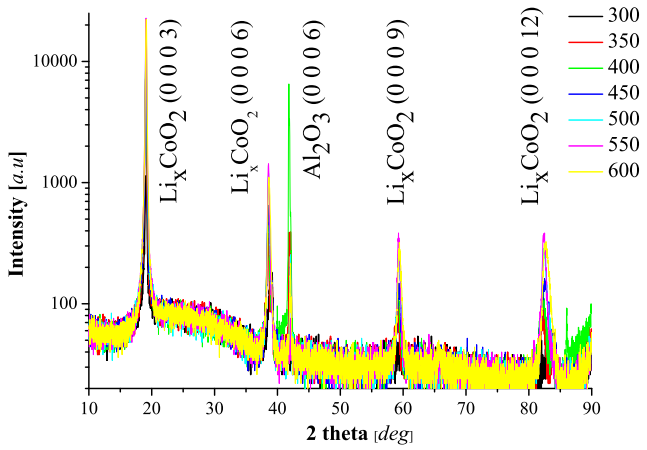

Fig. 1. (Free of charge) XRD patterns of Li_xCoO_2 thin films deposited in the temperature range of 300–600 °C.

under Ar atmosphere and is followed by a first reaction of the well ground powders at 750 °C for 12 h. The resulted fine $LiCoO_2$ powder was then cold pressed into a target at 0.4 GPa for 10 min. The produced 15 mm target was sintered at 900 °C for 16 h, with heating and cooling rate of 100 °C/h.

2.2. Thin film growth

Li_xCoO_2 thin films were grown on both pristine (0 0 0 1) Al_2O_3 and Cr/Au sputter coated (0 0 0 1) Al_2O_3 substrates using the PLD technique. To improve the surface quality of the films, (0 0 0 1) Al_2O_3 single crystals with step terraces were used as substrates for the growth, obtained by annealing the as–received commercial substrates at 1200 °C for 1 h in air as proposed by Yoshimoto et al. [7]. Metal films composed of Cr (20 nm)/Au (80 nm) were deposited on (0 0 0 1) Al_2O_3 substrates by DC sputtering and used as electrodes to perform conducting probe (CP)–AFM measurements and surface modifications, similar to those conducted by Schneegans et al. in Na_xCoO_2 [8] compound and are presented elsewhere [9].

A KrF laser (COMPexPro 201, $\lambda = 248$ nm and $\tau = 25$ ns) operated at 1 Hz was used to ablate the target at an angle of 45°, with a total number of 1000 pulses per film. The focused spot size was $2 \times 5\,mm^2$ on the target resulting in a fluence of ~1.1 J/cm^2. The target was placed 37 mm away from the substrate and was rotated around its center at 20 rpm during the deposition to keep the ablated target surface fresh. Prior each deposition the chamber was evacuated to a base pressure $< 5 \times 10^{-6}$ mbar. During the deposition process the oxygen pressure in the chamber was kept constant at 1 mbar. Films were grown at different substrate deposition temperatures in the range of 300–600 °C with a temperature step of 50 °C, using heating and cooling rate of 10 °C/min. The thickness of all the films was estimated to be approximately 100 nm, by using optical profilometry.

2.3. Characterization

The phase purity of the thin films and ceramic targets was studied by X-ray diffraction (XRD) using Cu K_α radiation (Shimadzu XRD-6000 diffractometer) in a Bragg–Brentano geometry, where

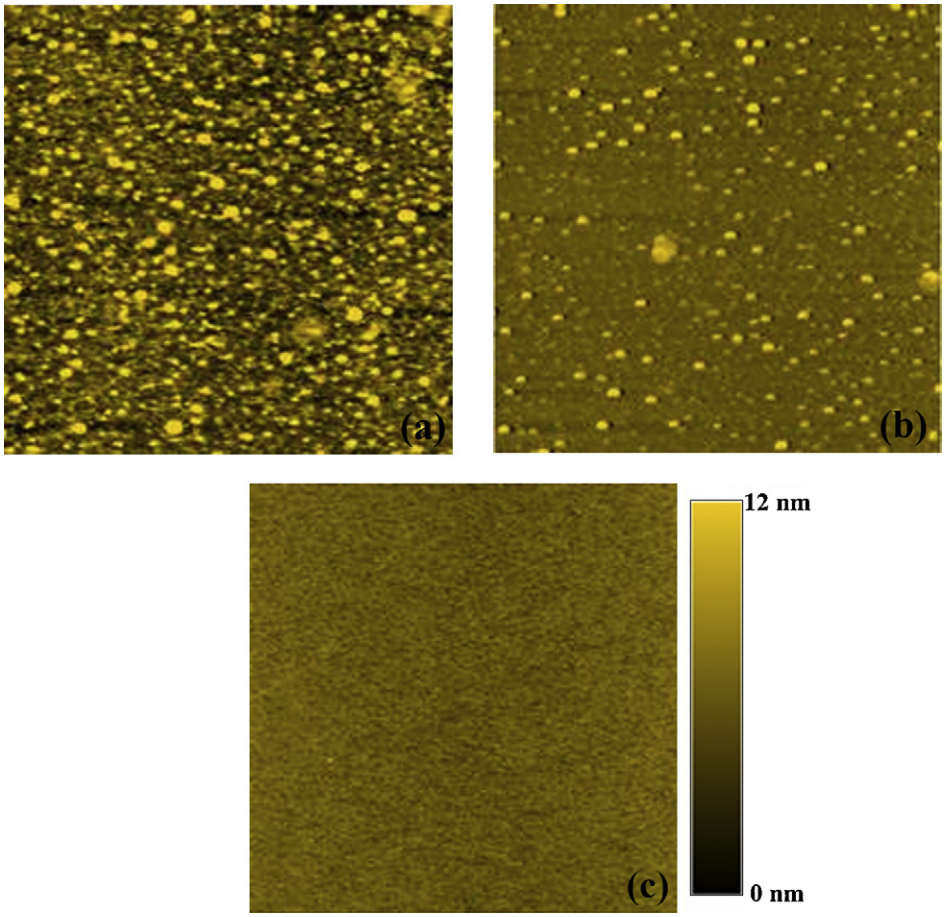

Fig. 2. (Free of charge) AFM images ($10 \times 10\,\mu m^2$) of Li_xCoO_2 thin films deposited at (a) 400, (b) 500 and (b) 600 °C, respectively. The R_a has changed from 3.7 to 0.7 nm by increasing the deposition temperature. The scale is the same for all three images.

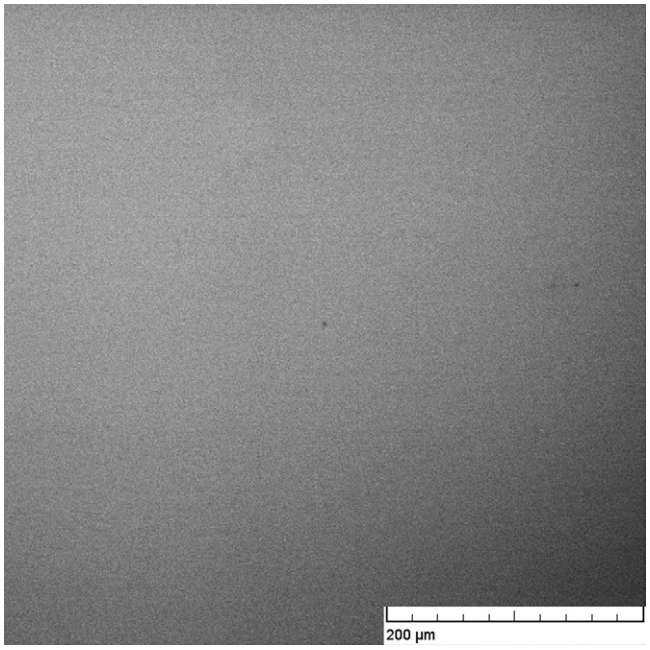

Fig. 3. Secondary electron image of the Li_xCoO_2 film deposited at 600 °C with a large field of view.

θ–2θ scans were performed. The morphology of the films in large areas of the surface was examined by scanning electron microscopy (SEM; Tescan Vega II LSU). Furthermore the surface morphology and the electrical properties of the thin films were examined in detail with a homemade CP–AFM. Both the tip and the cantilever, used in the study of the surfaces, were conductive. When the probe was brought in contact with the sample, the explored surface was scanned line by line. The probe-surface applied force was held constant (typically a few 10^{-9} to a few 10^{-8} N) and a bias voltage was applied between the probe and the sample (up to few *V*). The resulting current measured by the conversion system reflects the local tip/sample contact resistance [8]. By recording synchronously the conversion system output voltage and the height values along each scan line, the topographical and electrical map of the studied area were simultaneously investigated.

3. Results and discussion

The influence of the deposition temperature on both the surface morphology and crystallinity of the grown films was investigated. To this end the films prepared at different deposition temperatures were investigated using both XRD and AFM. Fig. 1 displays the XRD patterns of the deposited thin films. The patterns exhibit intensive (0 0 0 *l*) Bragg peaks of Li_xCoO_2 with no evidence of secondary phases such as Co_3O_4 *etc.* within the resolution of the instrument used. The appearance of all and only the (0 0 0 *l*) reflections is clear evidence for the HT–phase formation and the strong orientation of the films along the *c*-axis [6].

The surface roughness of the films was evaluated over an area of $10 \times 10\,\mu m^2$ using AFM. Fig. 2(a) is an AFM image of the film deposited at 400 °C showing that the film is free of cracks, holes or island structures with $R_a \sim 3.7$ nm. Fig. 2(b) and (c) are AFM images of the films deposited at 500 and 600 °C, respectively. The surface roughness has been reduced ($R_a \sim 2.7$ and 0.8 nm, respec-

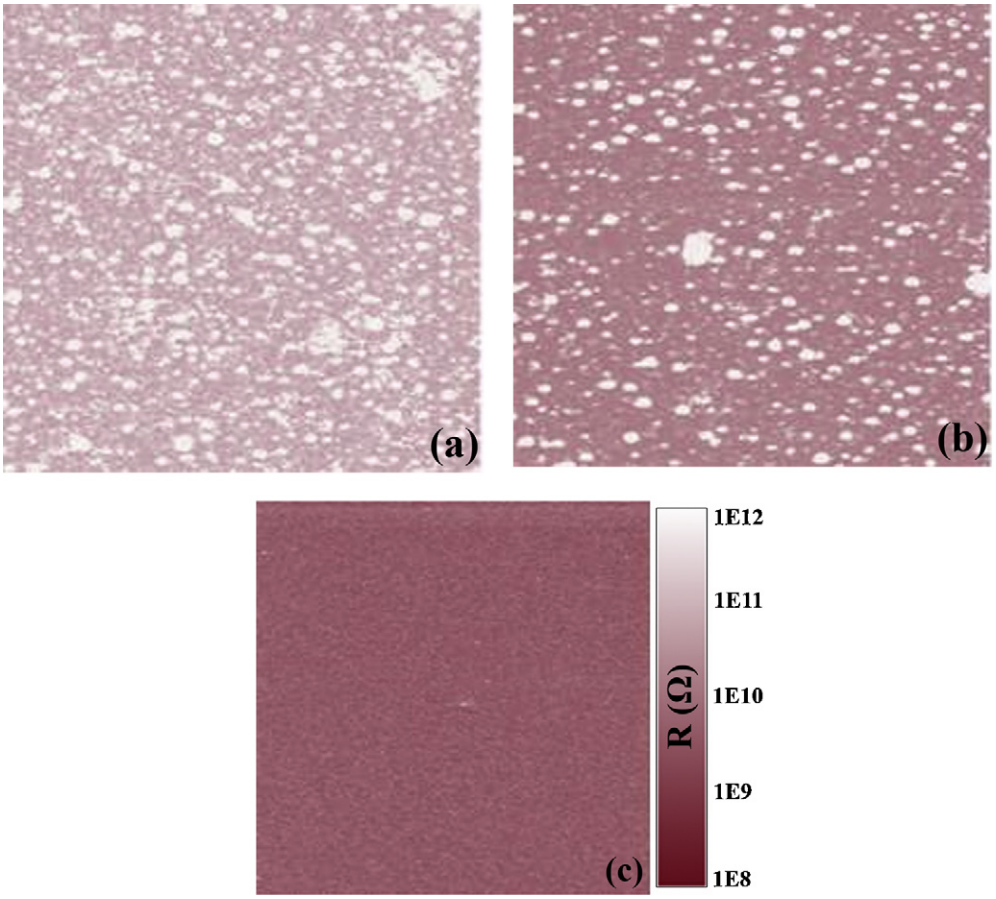

Fig. 4. (Free of charge) CP–AFM images ($10 \times 10\,\mu m^2$) of the Li_xCoO_2 films deposited at (a) 400, (b) 500 and (c) 600 °C, respectively. The surface resistance decreases as the deposition temperature increases. The scale is applicable to all three CP–AFM images.

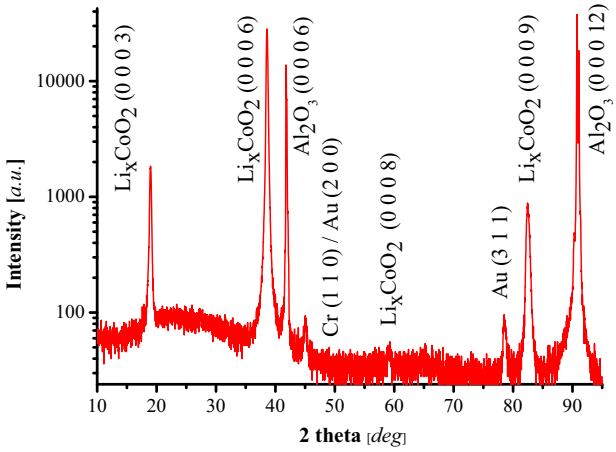

Fig. 5. (Free of charge) XRD pattern on the Li_xCoO_2 thin film deposited at 400 °C on Cr/Au coated (0 0 0 1) Al_2O_3. Extra peaks appearing in the pattern are attributed to Cr and Au thin films. The Li_xCoO_2 thin film is strongly (0 0 0 *l*) oriented.

tively) compared to the film deposited at lower temperatures and can be attributed to enhanced surface diffusion. This suggests that the roughness of the films can be reduced by performing growth at higher temperatures. The AFM results on the change of the morphology are in good agreement with SEM imaging that was performed on large surface areas. Fig. 3 is a secondary electron image of a film deposited at 600 °C over a large area with a field of view of 500 μm.

The Li_xCoO_2 thin films produced in the current study were further investigated by CP–AFM over areas of $10 \times 10\ \mu m^2$. The surface resistance map investigations of the thin films produced at 400, 500 and 600 °C are presented in Fig. 4(a), (b) and (c), respectively. The resistance mappings shown in Fig. 4(a), (b) and (c) were made at the same locations where the surface roughness had also been determined (Fig. 2(a), (b) and (c), respectively) in order to correlate the surface roughness with the surface resistance. It can be easily deduced that the rough areas of the film surfaces exhibit higher resistance and also the surface resistance is more uniform over the entire area of the smoother films. In addition, by increasing the deposition temperature not only the average surface roughness is being reduced, but also there is a 4 orders of magnitude reduction in the surface resistance of the films. The strong modification of the surface resistance as a function of the deposition temperature could be attributed to several factors such as change in carrier concentration and/or crystallinity of the films. The change in carrier concentration could be related to a change in Li-concentration and can be investigated both with high-resolution XRD and also Hall resistivity measurements. The issue of crystallinity can be attributed to simultaneous presence of HT and other minor phases and can be investigated with high-resolution XRD measurements. Both of these factors are currently under investigation.

The deposition temperature of 400 °C was selected for further investigation because the surface roughness, obtained at this relatively low temperature, is reasonable. The XRD pattern shown in Fig. 5 is from a Li_xCoO_2 film deposited on a Cr/Au sputter coated (0 0 0 1) Al_2O_3 substrate. Cr is deposited as an adhesion layer due to the poor adhesion of Au on oxide single crystal surfaces. Extra peaks appearing in the XRD spectrum of Fig. 5 are attributed to the Cr and Au metal layers. The orientation of the thin films is also in the (0 0 0 *l*) direction, despite the presence of the electrode thin metal film. We believe that the compound has a tendency to grow along the *c*-axis under the present deposition conditions with no strong dependence on the type of substrate used. The structure of the initial surface of the substrate will affect the possible epitaxial growth of the thin film. Such composite films are currently under investigation, revealing new exotic phenomena with possible use in advanced electronics, and have been reported elsewhere [9].

4. Conclusions

We report a one-step approach for the growth of smooth, *c*-axis oriented HT–phase Li_xCoO_2 thin films on bare and Au/Cr coated (0 0 0 1) Al_2O_3. The deposition temperature dramatically changes the surface morphology and surface resistivity of the films. The HT–Li_xCoO_2 thin films grown on atomically flat (0 0 0 1) Al_2O_3 substrate at 600 °C have very low surface roughness and resistance. We believe that the growth at relatively high oxygen pressures is a promising method for obtaining high quality HT–Li_xCoO_2 thin films.

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