



LiFePO₄ thin films grown by pulsed laser deposition: Effect of the substrate on the film structure and morphology

V. Palomares^a, I. Ruiz de Larramendi^a, J. Alonso^b, M. Bengoechea^c, A. Goñi^a, O. Miguel^c, T. Rojo^{a,*}

^a Departamento de Química Inorgánica, Facultad de Ciencia y Tecnología, Universidad del País Vasco, Apdo. 644, 48080 Bilbao, Spain

^b Departamento de Electricidad y Electrónica, Facultad de Ciencia y Tecnología, Universidad del País Vasco, Apdo. 644, 48080 Bilbao, Spain

^c CIDETEC-IK4, P^o Miramón 196, 20009 Donostia-San Sebastián, Spain

ARTICLE INFO

Article history:

Received 8 May 2009

Received in revised form 24 September 2009

Accepted 30 October 2009

Available online 10 November 2009

Keywords:

LiFePO₄

Pulsed laser deposition

Conductive substrates

ABSTRACT

Well crystallized and homogeneous LiFePO₄/C (LFPO) thin films have been grown by pulsed laser deposition (PLD). The targets were prepared by the sol–gel process at 600 °C. The structure of the polycrystalline powders was analyzed with X-ray powder diffraction (XRD) data. The XRD patterns were indexed having a single phase olivine structure (Pnma). LFPO thin films have been deposited on three different substrates: aluminum (Al), stainless steel (SS) and silicon (Si) by pulsed laser deposition (PLD). The structure of the films was analyzed by X-ray diffraction (XRD), Raman spectroscopy, scanning electron microscopy (SEM), transmission electron microscopy (TEM) and atomic force microscopy (AFM). It is found that the crystallinity of the thin films depends on the substrate temperature which was set at 500 °C. When annealed treatments were used, secondary phases were found, so, one step depositions at 500 °C were made.

Stainless steel is demonstrated to be the best choice to act as substrate for phosphate deposition. LiFePO₄ thin films grown on stainless steel plates exhibited the presence of carbon, inducing a slight conductivity enhancement that makes these films promising candidates as one step produced cathodes in Li-ion microbatteries.

© 2009 Elsevier B.V. All rights reserved.

1. Introduction

Olivine LiFePO₄ is considered one of the most promising materials to substitute present LiCoO₂ as cathode for secondary lithium ion batteries. Due to this fact, it has been thoroughly studied for the last 10 years, from the synthesis processes [1–13], to its electrochemical behaviour [14–25]. Now, a new branch of study emerges, the thin film approach.

The fabrication of microscale batteries has arisen as a desirable objective in the last 25 years due to the great advances made in the microelectronic field. The boost in the production of small size devices, such as CMOS (Complementary Metal Oxide Semiconductors), FE-RAM (Ferroelectric Random Access Memory), liquid crystal screens, microcomputers, MEMs (Micro Electronic Memories) and medical implants has reinforced the search for micro-sized energy-containing devices.

In the last years, some experiments have been carried out using different techniques in order to get the desired thin films, such as electrostatic spray deposition [26], bias sputtering [27] and radio frequency sputtering [28,29]. But the most used procedure is pulsed laser deposition (PLD) [30–37].

In this work, we have prepared several LiFePO₄ (LFPO) thin films by PLD and studied the effect of the different deposition parameters on the crystallinity and porosity of the samples. Two different substrates were selected for LFPO thin films deposition so they could be used as current collector, in order to test the as-produced films without further preparation. The selected substrates were aluminum and stainless steel. These materials are electronic conductors, withstand LFPO phase crystallization temperature, compatible with the electrolyte and the other components of the battery, being not exceedingly expensive. Silicon single crystals were also used as substrates to produce thin films for their easier characterization, in spite of their insulator character and the impossibility of epitaxial growth. X-ray diffraction (XRD), Raman spectroscopy, atomic force microscopy (AFM), scanning electron microscopy (SEM), transmission electron microscopy (TEM) and room temperature conductivity DC four-probe measurements have been performed.

2. Experimental

2.1. PLD target preparation

LiFePO₄ powder samples were prepared by a sol–gel method, using stoichiometric amounts of citric acid hydrate (C₆H₈O₇·H₂O), ferrous acetate (FeC₄H₆O₄), lithium hydroxide hydrate (LiOH·H₂O)

* Corresponding author. Tel.: +34 94 6012458; fax: +34 94 6013500.

E-mail address: teo.rojo@ehu.es (T. Rojo).

Table 1

PLD deposition parameters of the LiFePO₄ thin films (Al: aluminum; SS: stainless steel; Si: silicon).

Thin film	Substrate	Temperature (°C)	Time (min)
Al1	Al	Room temperature	30
Al1A	Al	Al1 + annealed at 500 °C	30
SS1	SS	Room temperature	30
SS1A	SS	SS1 + annealed at 500 °C	30
SS2	SS	500 °C	30
SS3	SS	500 °C	60
Si1	Si (100)	500 °C	30

and ammonium dihydrogenophosphate (NH₄H₂PO₄) with a molar ratio of 1:1:1:1. The reagents were dissolved in 25 ml water and the resulting solutions were heated and stirred until gel formation occurred. The gels were annealed at 350 °C to decompose the salts, then pressed into pellets, and calcined at 750 °C under nitrogen flux, in order to crystallize the desired phase and to obtain well sintered pellets. All targets showed black colour, due to their carbon content, which was of about a 10% weight.

The targets were characterized by X-ray powder diffraction data, collected using a Philips PW1710 and Bruker D8 Advance Vario diffractometers, with CuK_α radiation, and fitted using the FULLPROF program [38,39].

2.2. Thin films preparation

Using the sintered pellets as targets, LFPO films have been deposited on aluminum, stainless steel and Si single crystal substrates by PLD (see Table 1). The samples were deposited using a LAMBDA PHYSIC Compex 102 KrF excimer laser (248 nm, 130 mJ/pulse) at a frequency of 15 Hz. The target was placed in a rotating target holder in a vacuum chamber with an initial pressure of 2×10^{-6} mbar. The substrates were mounted on a heater and the films were deposited at room temperature and at a substrate temperature of 500 °C, taking into account the existing literature [40,41] and our previous experience in PLD [42]. Argon gas was flowed into the chamber in a constant flux during deposition, keeping a pressure of 8×10^{-2} mbar. Deposition times were 30 and 60 min. An additional thin film was deposited at room temperature on an Al substrate and annealed ex situ in nitrogen atmosphere at 500 °C for 3 h in order to check whether an ex situ annealing was more adequate than growing the film at high temperature or not. Table 1 shows the PLD deposition parameters for obtained thin films.

2.3. Characterization of the thin films

X-ray powder diffraction data were used to characterize the obtained films, using a Philips PW1710 (Bragg–Brentano geometry) diffractometer, with CuK_α radiation, and fitted with the FULLPROF program [38,39]. In order to study the C content in the films Raman measurements were carried out at room temperature by using a InVia Renishaw RA100 spectrometer equipped with a Leica microscope DMLM. The 514 nm light from an Ar-ion laser was employed as excitation radiation. The spectra were recorded with the average of 10 scans and 20 mW power. The atomic force microscopy (AFM) measurements were performed using a commercial scanning probe microscope (Nanotec DSP classic). The microstructure of the obtained films was observed by scanning electron microscopy (SEM) using a JEOL JSM-6400 microscope at 20 kV accelerating voltage and transmission electron microscopy (TEM) with energy dispersive X-ray (EDX) spectroscopy using a Philips CM200.

The conductivity of the SS2 film was measured in air at room temperature by a DC four-probe technique. In order to prevent substrate influence on conductivity measurements, a glass

substrate was employed to produce an analogous thin film in the same experimental conditions as SS2. Electrical contacts were made using Pt wires and Pt paste placed over whole end faces ensuring a homogeneous current flow.

3. Results and discussion

3.1. Sample and thin films characterization

The X-ray diffractogram of the target obtained at room temperature by sol-gel is shown in Fig. 1. All the diffraction peaks were indexed for the LiFePO₄ olivine structure [43], without the appearance of any unknown diffraction maximum.

X-ray diffraction patterns of the thin films deposited on Al substrates at room temperature and annealed at 500 °C are shown in Fig. 2. A complete crystallization of the LiFePO₄ phase on Al substrate at room temperature was not obtained. This film also presents the presence of secondary reflections due to the presence of the LiAlO₂ phase (see Fig. 2a). When the thin film is deposited at room temperature and then annealed at 500 °C, some small peaks corresponding to the LiAlO₂ secondary phase were also found. The peak observed at 22.3° (2θ) corresponds to the highest intensity peak for LiAlO₂ phase. Thus, taking into account that the measured intensity for this peak is relatively low, it can be assumed that impurity amount is low, so it is difficult to distinguish the other

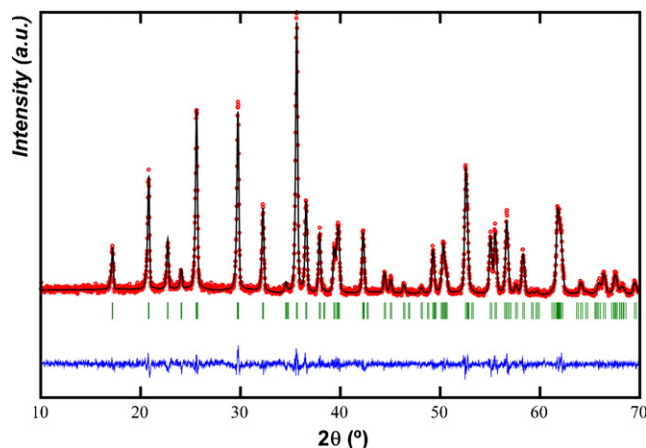


Fig. 1. XRD diffractogram and the fitted profile of LFPO phase of the target and experimental (circles), fitted (line) and difference between them (lower line).

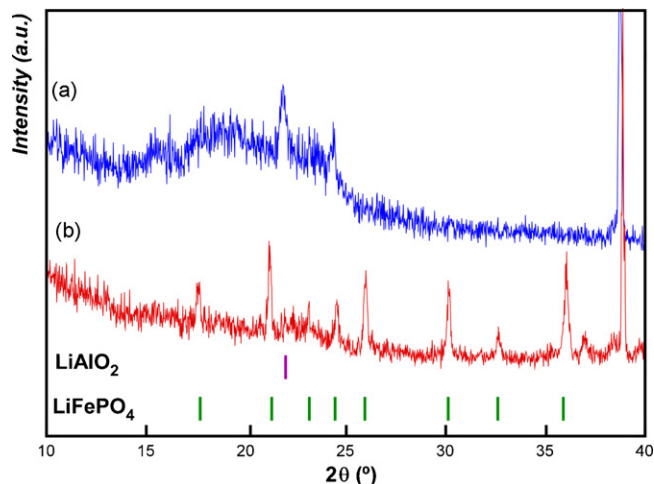


Fig. 2. XRD patterns of LFPO films obtained at (a) room temperature (Al1) and (b) annealed at 500 °C (Al1A) on Al substrates.

Download English Version:

<https://daneshyari.com/en/article/5363300>

Download Persian Version:

<https://daneshyari.com/article/5363300>

[Daneshyari.com](https://daneshyari.com)