Applied Surface Science 368 (2016) 173–176

Contents lists available at ScienceDirect

Applied Surface Science

journal homepage: www.elsevier.com/locate/apsusc

Lithium titanium oxynitride thin film with enhanced lithium storage and rate capability

Zhaozhe Yu[a,b,*], Huarui Xu[a,b,*], Guisheng Zhu[b], Dongliang Yan[b], Aibing Yu[c]

[a] School of Microelectronics and Solid-State Electronics, University of Electronic Science and Technology of China, Chengdu 610054, China
[b] Guangxi Key Laboratory of Information Materials, Guilin University of Electronic Technology, Guilin 541004, China
[c] Department of Chemical Engineering, Monash University, Clayton, 3800, VIC, Australia

ARTICLE INFO

Article history:
Received 6 November 2015
Received in revised form 18 January 2016
Accepted 30 January 2016
Available online 2 February 2016

Keywords:
Lithium ion battery
Anode
High rate capability
Lithium titanium oxynitride thin film
Powder sputtering technique

ABSTRACT

The lithium titanium oxynitride (LTON) thin film electrode was prepared by radio frequency (RF) magnetron sputtering deposition using a cubic spinel structure $Li_4Ti_5O_{12}$ (LTO) powder target in a N_2 atmosphere for lithium ion batteries. XRD and SEM test results showed that the thin film was composed of weak crystal or amorphous structure and that its surface was homogeneous. XPS analyses indicated that nitrogen atoms were actually incorporated into the LTO matrix framework. The substitution of nitrogen for oxygen in the thin film created more abundant cross-linking structures, which favored the higher mobility of lithium ions. The LTON had a high capacity of 290 mAh g^{-1} at 0.1C, excellent rate capability of 160 mAh g^{-1} at 5C and only ≈7% capacity loss after 100 cycles at 5C charge and discharge rate. These properties make this thin film electrode a promising candidate material for use in thin film lithium ion batteries.

1. Introduction

Rechargeable lithium ion thin film batteries (TFBs) will find a potential application as a power source in the miniaturization of electronic devices [1–4]. During the last years, lithium titanium oxide (LTO) has been prepared for thin film rechargeable lithium ion batteries. However, the rate capability of LTO is relatively low because of its poor electronic conductivity (<10^{-13} S cm^{-1}) and sluggish lithium ion diffusion [5,6]. The properties of LTO might not be sufficient for high current applications before any materials modifications.

It has been recently reported that the nitridation of the Ti-based compounds (LTO and TiO_2) can form a more conductive TiO_xN_y species [7–10]. The highly conducting TiO_xN_y provide a short lithium ion diffusion length and a high electronic conductivity along the surface. Unfortunately, thin TiO_xN_y layers covered on the surface can just improve the electrical conductivity of the surface of LTO or TiO_2. There is no significant contribution to the internal mass transfer capability. If TiO_xN_y species are formed inside the LTO thin film, it will significantly improve electronic conductivity and enhance lithium storage capacity. So in this article we report a successful preparation of amorphous LTON thin films by using RF magnetron sputtering in a N_2 atmosphere with a LTO powder target.

2. Experimental

2.1. Preparation of electrodes

The LTO powder ($Li_4Ti_5O_{12}$, >99%, Btr New Energy materials INC, Shenzhen, China) was dried at 120 °C over 10 h. The powder was pressed into a copper target holder (70 mm in diameter) with 5 ton uniaxial presses. No further processes were involved in powder target production. The LTON thin film electrodes were deposited onto a stainless steel (SS) substrate using JPG-560C12 (SKY Technology Development Limited Company of Chinese Academy of Sciences, Shenyang, China) RF magnetron sputtering system. The SS substrate-target distance was 70 mm. The substrate was held at 400 °C during the deposition. LTON thin film with a thickness of 110 nm was prepared by sputtering for 2 h at an applied power of 80 W in a high-purity N_2 atmosphere of 1.6×10^{-2} mbar pressure. Films were annealed after deposition in flowing Ar at 700 °C for 2 h. The film electrode mass are measured by high precision analytical balance.

* Corresponding authors at: University of Electronic Science and Technology of China, School of Microelectronics and Solid-State Electronics, Construction Road 2 Paragraph 4, Chengdu 610054, China. Tel.: +86 773 2230256; fax: +86 773 2291159.
E-mail addresses: yuzhaozhe@126.com (Z. Yu), huaruixu@guet.edu.cn (H. Xu).

http://dx.doi.org/10.1016/j.apsusc.2016.01.284
0169-4332/

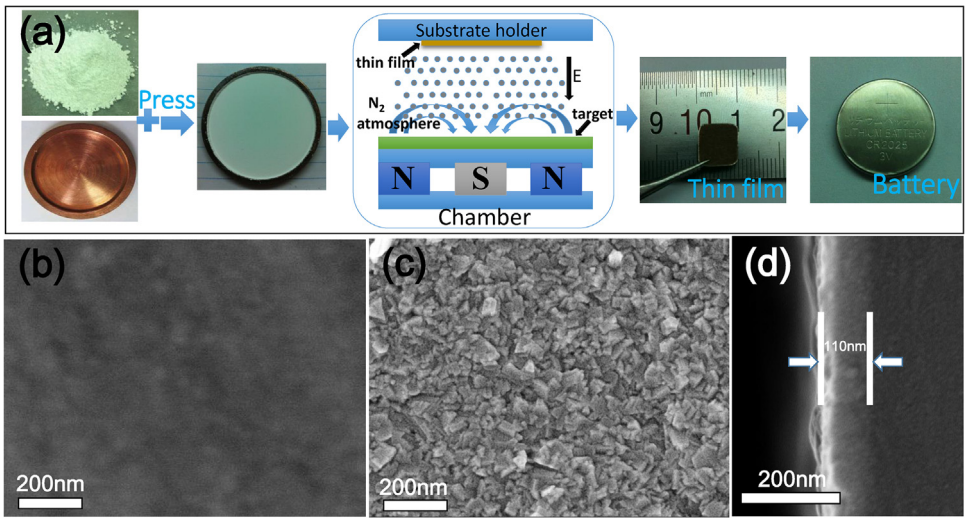

Fig. 1. (a) Schematic illustration for the fabrication of LTON. (b) and (c) SEM images of as-deposited LTON and annealed LTON. (d) Cross-sectional SEM images of LTON.

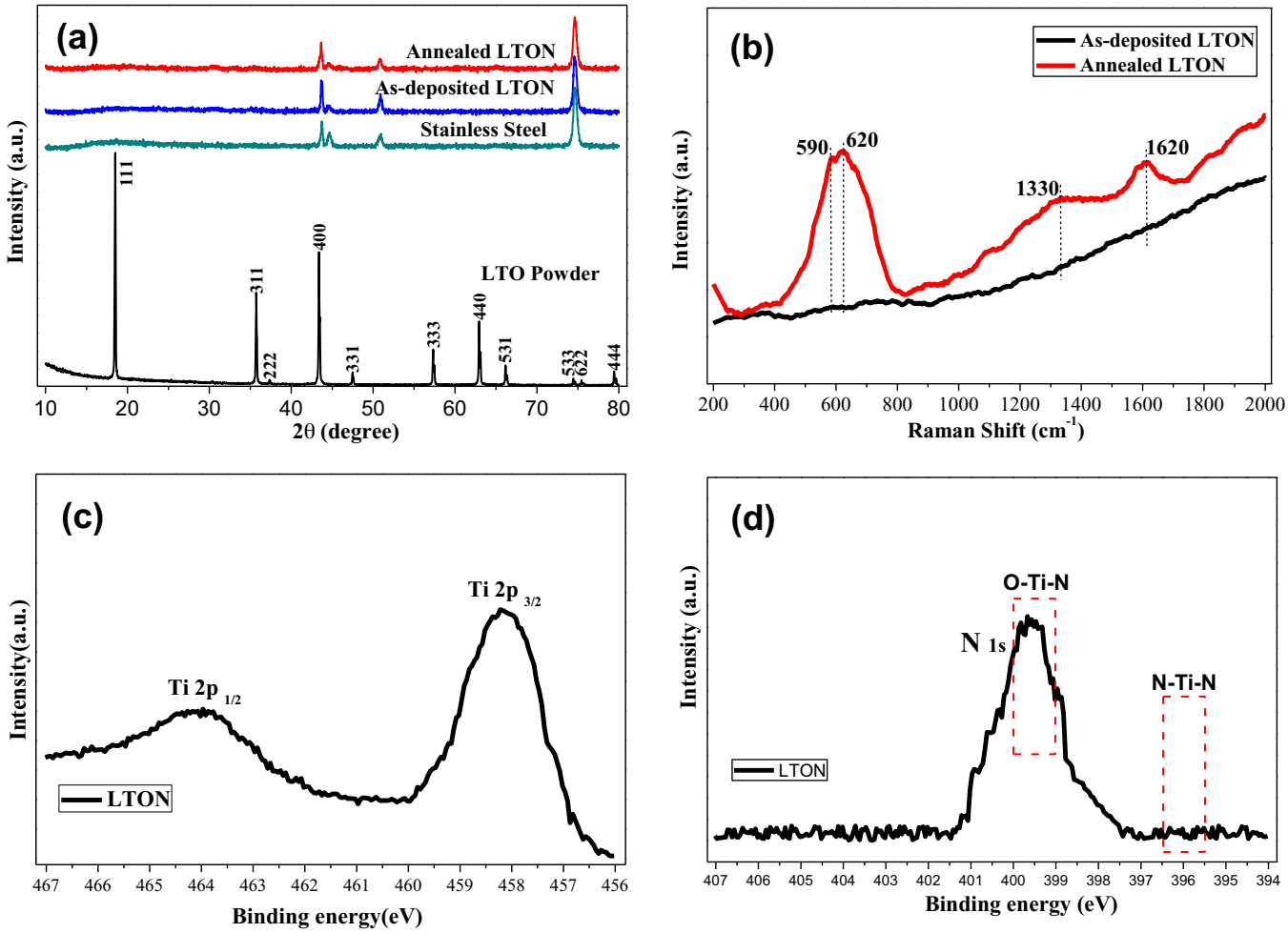

Fig. 2. (a) XRD pattern of Powder target、SS、as-deposited and annealed LTON thin films. (b) Raman spectra of as-deposited and annealed LTON thin films. (c) and (d) Overlay of normalized Ti_{2p} and N_{1s} core level XPS spectra of LTON.

2.2. Characterization of materials

The crystal structure of the obtained samples was characterized by X-ray diffraction (XRD, Rigaku DMAX 2500, Tokyo, Japan) using Cu *Kα* radiation, Raman spectra (JY Labram HR 800) and X-ray photoelectron spectroscopy (XPS, thermo ESCALAB 250Xi spectrometer) using Al *Kα* (at 1486.6 eV) as the X-ray source. The microstructural properties were characterized using scanning electron microscopy (SEM) (SEM, Hitachi S-4800, Tokyo, Japan).