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All-solid-state microscale lithium-ion battery fabricated by a simple process with graphene as anode

Jie Lin, Yuling Wu, Ruike Bi, Hang Guo*

Pen-Tung Sah Micro-Nano Science and Technology Institute, Xiamen University, Xiamen, Fujian 361005, China

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ABSTRACT

Few works directly utilize monolayer or few-layer Graphene in energy storage because of the limited active materials. But it can be exploited in micro-power sources with low-rise power requirement, especially the microscale thin film lithium-ion batteries (MBs). Here a simple micro-fabrication process including one-step magnetron sputtering, is developed for fabricating the MBs with the ultrathin Graphene as anode. The footprint area of a single battery is ~1 mm^2 and the total thickness is ~600 nm. In the MBs, lithium cobalt oxide ($LiCoO_2$) and lithium phosphorous oxynitride (LiPON) films are used as the cathode and electrolyte, respectively. This work provides guidance to manufacture high performance micro-power devices using advanced materials by a simple process.

1. Introduction

Advances in lithium-ion batteries (LIBs) have trigged great improvements in portable devices [1] especially in micro-power sources for micro electro mechanical systems (MEMS) [2]. But most LIBs are assembled in bulk configurations (columnar, square, coin, etc.), restricting the wide application and integration in microscale devices. Thus, thin film LIBs with all-solid-state [3] and flexible structure [4] are proposed to solve the issue. Historically, Bates et al. [5,6] firstly invented the thin film LIBs with lithium phosphorous oxynitride (LiPON) and lithium cobalt oxide ($LiCoO_2$) as electrolyte and cathode, respectively; Baggetto et al. [7,8] optimized the two-dimensional (2D) thin film LIBs by using three-dimensional (3D) Si substrate and presented 3D thin film LIBs; West et al. [9] fabricated microscale thin film LIBs (MBs) through MEMS techniques; Fu et al. [10] generally employed and summarized various thin film materials for thin film LIBs; Song et al. [11] made use of aluminum as the anodes of thin film LIBs for powering MEMS devices. These works have pushed our understanding of how to apply bulk battery technology into micro-power sources, and we further aim at easily utilizing advanced materials into MBs.

Recently, increased interests have been attached on two-dimensional (2D) materials [12,13], especially Graphene [14], due to the high electrical conductivity, specific surface area and mechanical properties. Graphene can be used as the electrode because of the high conductivity and high lithiation capacity, meaning that higher energy density can be achieved in the LIBs with Graphene as anode. Also, the volume or mass of Graphene [14] is so small compared to conventional electrodes, that largely contributes to the total energy density of whole battery with higher space utilization. Moreover, the lithiation capacity of Graphene [15,16] depending on various intercalation mechanisms is far higher than the most widely used graphite anode (397 mAh g^{-1}) [17]. As a result, the utilization of Graphene in LIBs, especially in MBs, is significant for developing high performance power sources. Micro-fabrication techniques including lithography, deposition, etching, peeling, etc. [18] are widely used in microelectronic industry, which are advantageous for the further integration of MBs in on-chip devices [11].

In this work, a simple process is developed for utilizing the Graphene film deposited by chemical vapor deposition (CVD) in MBs as the anode. The effective area of a single MB is limited as ~1 mm^2 through lithography and lift-off process. Also, all compounds except Graphene are fabricated by one-step continuous magnetron sputtering, providing the feasibility of effective and mass production. Furthermore, the MBs are packaged in semiconductor device cases, and tested by electrochemical measurements, exhibiting apparent voltage plateaus and excellent performance.

* Corresponding author.
E-mail address: hangguo@xmu.edu.cn (H. Guo).

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Table 1
Deposition conditions of all films fabricated by magnetron sputtering.

Materials	Target	Mode	Power (W cm^{-2})	Pressure (Pa)	Atmosphere	Thickness (nm)
LiPON	Li_3PO_4	RF	1.27	1.3	N_2 = 100%	180
$LiCoO_2$	$LiCoO_2$	RF	1.53	1.5	O_2:Ar = 1:3	230
Al	Al	DC	1.27	1.3	Ar = 100%	200

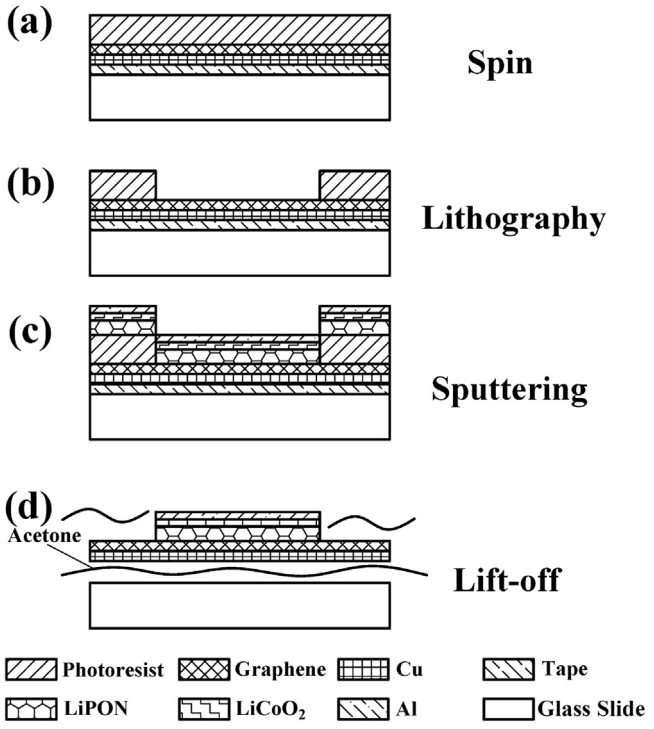

Fig. 1. Micro-fabrication process of MBs with Graphene as anode: (a) spinning photoresist, (b) ultra-violet lithography, (c) magnetron sputtering and (d) Lift-off of excessive films.

2. Methods

2.1. Fabrication

The micro-fabrication process of the MBs using Graphene as anode material are schematically illustrated in Fig. 1. Firstly, the Graphene was grown on the pocket of Cu foils at 1030 °C by CVD method with a mixture of 10-sccm methane and 10-sccm hydrogen for ~20 min on a tube furnace. Secondly, the sample was attached on a glass slide (or Si wafer, stainless steel, etc.) with tape, and patterned with positive photoresist BP212, and lithographed to define the effective areas. Thirdly, the solid electrolyte, cathode and current collector of LiPON, $LiCoO_2$ and Al films were consecutively sputtered on Graphene using JC500-3D magnetron sputtering system. The sputtering parameters for different films are listed in Table 1. Finally, after the lift-off of excessive films in acetone, the MBs are obtained as shown in Fig. 2.

2.2. Packaging and tests

Approximately 100 individual MBs were fabricated on per 3cm × 3 cm Graphene as depicted in Fig. 2a. The samples were separated in 4 MBs per unit, and attached on semiconductor device bases. Subsequently, they were connected with external circuits through ultrasonic bonding with Al wires (Fig. 2b). The metallic protective caps were placed over the MBs, and the devices were then sealed in the glovebox filled with argon (Fig. 2c). Finally, the cells were connected with a four-probe micro manipulative station, and tested by using Arbin BT2000 test instruments with a charge/discharge current density of 50/10 nA per MB between 0.1 and 2 V.

The surface and cross section morphologies were investigated by using ZEISS Sigma scanning electron microscopy (SEM). The Raman spectra (WITec Alpha-300) were obtained with a 488-nm laser excitation wavelength. The electrochemical properties of $LiCoO_2$ and Graphene films deposited on Al and Cu foils respectively, were assembled with lithium counter electrodes in coin cells in an argon-filled glove box, and the electrolyte was 1.0 mol L^{-1} $LiPF_6$ solution mixed with ethylene carbonate/ethylmethyl carbonate/diethyl carbonate (EC/EMC/DEC = 1:1:1 in volume). After the half-cells were shelved for ~12 h, the galvanostatic charge/discharge tests were conducted on Neware BTS-5 V/1 mA battery test systems. The current density was 20 and 50 μA cm^{-2}, and the voltage window for cycling was 0.01–3 and 3–4.2 V, for anode and cathode, respectively.

3. Results and discussion

3.1. Structural characterization

After transferred to an oxidized Si wafer through a wet chemical etching process, the Raman spectra of the Graphene deposited on Cu foil is detected. The corresponding Raman spectra is mainly composed of four peaks: The D-band at ~1328 cm^{-1} is attributed to the first-order scattering induced by the disorder interlayer effects, the G-band at ~1583 cm^{-1} is related to the in-plane vibrations of

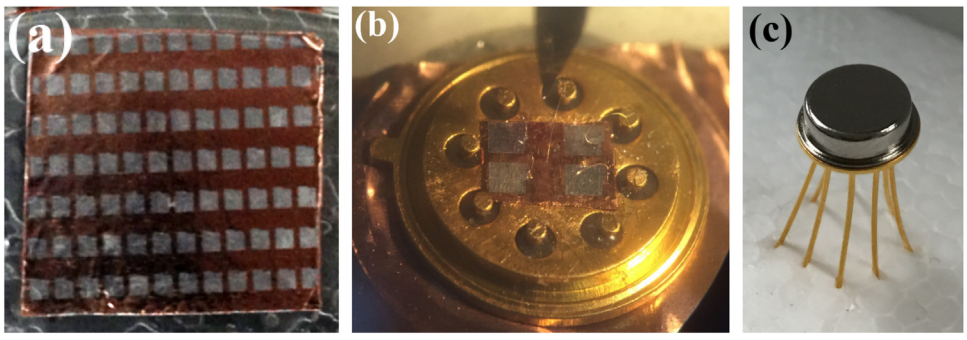

Fig. 2. Optical images of (a) prepared, (b) bonding and (c) packaged MBs with Graphene as anode.

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