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The influence of change in structural characteristics induced by beam current on mechanical properties of LiPON solid-state electrolyte films

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ABSTRACT

Lithium phosphorus oxynitride (LiPON) solid-state electrolyte films were synthesized by ion beam assisted deposition (IBAD) system from Li_3PO_4 target in nitrogen reactive plasma. Extensive measurements were taken to investigate the change in structural characteristics caused by beam current as well as the effects on mechanical properties of LiPON films. The existence of the triply coordinated nitrogen atoms in structure of LiPON films induced by ion beam bombardment was proved by X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS), which can produce the positive effects on Li^+ mobility. Analysis of nanoindentation indicated that the hardness and elastic modulus of LiPON solid-state electrolyte films varies with the beam current. The highest hardness of 5.8 GPa and the highest critical fracture load of 3.01 mN with lower compressive stress occurred at equal atomic percentage of nitrogen and phosphorus, i.e. N/P = 1 at the beam current of 18 mA. The higher hardness and lower stress are important parameters to prevent LiPON solid-state electrolyte films delamination from electrodes, which is crucial in evaluating the electrochemical performance of thin-film lithium ion battery.

1. Introduction

Thin-film lithium ion rechargeable batteries with the structure of current collector/anode/Li^+ solid-state electrolyte/Li^+ intercalation cathode/current collector/substrate have been investigated for their application in miniaturized ionic power devices such as electronic paper, smart cards, and RFID-Tag [1–3]. In order to improve performances of such micro-batteries, it is essential to optimize thin-film electrolyte's properties. During a charge/discharge cycle, the thin-film electrolyte must permit the high mobility transport of lithium ions between the anode and cathode while blocking the conduction of electrons [4]. This requires the deposition of

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films with an appropriate (lithium rich) chemistry and structure that has a high lithium ion mobility and is free of through thickness defects (such columnar pores or cracks) that provide electron discharge pathways when a voltage is applied between the electrodes [5].

All-solid-state lithium thin-film batteries have attracted significant research interest based on their application potential in Micro-electromechanical Systems (MEMS). As a solid electrolyte material, Lithium phosphorus oxynitride (LiPON) is a better candidate to be used as electrolyte film in all-solid-state thin-film batteries due to its dense, but high mobility amorphous structure [6,7]. For the applications, it is extremely important that LiPON electrolyte film, in addition high ionic conductivity, should be provided with desirable mechanical properties and adhesion ability to electrodes by appropriate synthesis techniques. However, most studies have focused on the study of the structure and electrochemical properties of LiPON films [8–12]. So far, few researches focused on hardness, elastic modulus, as well as residual stress/adhesion ability for solid-state electrolyte film. The influence of LiPON film deposition conditions on mechanical properties and adhesion ability is not clear. It is well recognized by the Li-ion battery community that stress can have a significant impact on the performance of the electrolyte [13]. Characterizing the mechanical properties of LiPON films plays a critical role because significant mechanical stresses develop in the electrolyte during charge and discharge cycling [14].

In order to optimize the chemistry, composition, and processing of solid electrolytes to withstand the stresses of charge and discharge cycling without compromising ionic conductivity, the future design and modeling of anode/solid electrolyte systems must address their mechanical properties [15]. Accordingly, the influence of deposition parameters on structure, composition and mechanical characters of LiPON films was investigated in this work. In this work, a low energy ion beam assisted deposition (IBAD) technique was explored for the synthesis of LiPON films. The IBAD approach uses an inert-gas ion beam to controllable sputter atoms from a Li_3PO_4 target and simultaneously bombarding the target with nitrogen ion beam provided by another ion gun. The influence of varying the beam current of nitrogen on structure, composition and mechanical characters of LiPON films was also investigated in this work.

2. Experimental

An IBAD system (FJL560CI2, Chinese Academy of Science) was used to synthesize LiPON films on Si (100) substrates. This system has two ion sources, one rotatable water-cooled sample holder and one rotatable water-cooled target holder (Fig. 1). The Li_3PO_4 target with an area of 69.5×69.5 mm^2 and 99.9 wt.% in purity was set at a 45-degree angle towards each substrate surface. Through computer control, we could rotate target to the sputtering working position and control the sputtering time. First of all, the substrates were cleaned in an ultrasonic agitator in acetone and alcohol for at least 15 min and dried using compressed air after each cleaning cycle. A second cleaning process was done in chamber of IBAD system in which the substrates were sputter-cleaned at vacuum for 5 min by Ar^+ (1.1 kV, 25 mA) bombardment. Then the introduction of Ar and N_2 gas to the ion source was controlled using the mass-flow controller, and the flow ratio of N_2 and Ar was 1:10. The Li_3PO_4 target was sputtered by Ar^+ and N^+ (1.1 kV) beams from sputtering ion source to deposit LiPON films. The base pressure of the vacuum chamber was 2.8×10^{-4} Pa. The deposition was carried out at a pressure of 1.2×10^{-2} Pa.

To evaluate the influence of ion beam current on the results, different beam currents (10, 12, 15, 18, 20 mA) were typically chosen to synthesize the LiPON films. All films were grown to a thickness of ~150 nm measured by an XP-2 surface profiler for 2 h. They were kept in a high purity Ar-filled glove box (<1 ppm H_2O and O_2), and all the test environment were kept clean and dry.

The phase structure of the films was investigated by X-ray diffraction (XRD) on a D/MAX 2500 diffractometer operated at 40 KV and 40 mA, with Cu Kα (40 kV, 20 mA, $\lambda = 0.15406$ nm) radiation in steps of 0.02°. The composition and the chemical state of LiPON solid-state electrolyte films were measured by X-ray photoelectron spectroscopy (XPS, PHI 5300 ESCA, USA).

The residual stress of the films was calculated applying the Stoney formula [16] by curvature measured using an XP-2 profiler. The hardness and elastic modulus and of the multilayers were measured using Nanoindenter XP system with a continuous stiffness measurement (CSM) technique. In this measurement, different from conventional indentation which can only do measurements at the unloading point, this technique allowed to measure the contact stiffness as well as the load and displacement at any point on the loading curve. Therefore, the hardness and elastic modulus can be continuously calculated as a function of indentation depth by analyzing means of a frequency specific amplifier data. The triangular Berkovich diamond indenter tip was calibrated using fused silica [17,18]. In this measurement, the Poisson ratio was 0.25; the maximum indentation depth was kept at 20–30% of the film thickness to minimize substrate effects. Each sample was indented ten times.

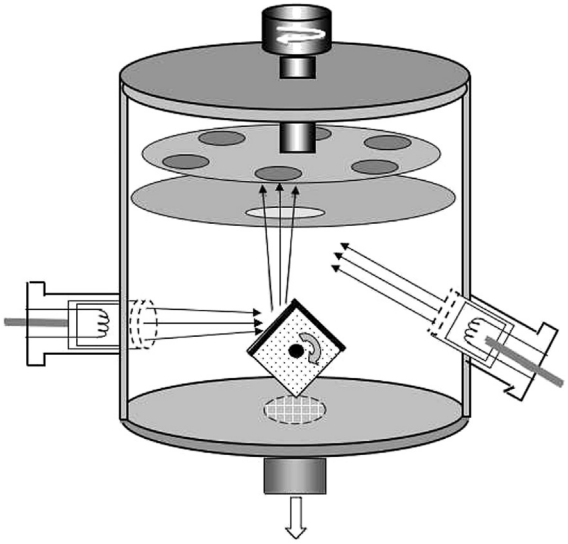

Fig. 1 – Schematic diagram of FJL560CI2 ion beam assisted deposition system.