X-ray Absorption Spectroscopy Approaches to Electronic State and Coordination Type of Lithium Phosphorus Oxynitride Thin Films

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In this study, lithium phosphorus oxynitride (LiPON) thin films were deposited by radio frequency (r.f.) magnetron sputtering of a lithium phosphate (Li₃PO₄) target with various powers. The crystal structure, morphology, chemical environment, ionic conductivity, electronic state and coordination type were sequentially characterized by X-ray diffraction, scanning electron microscope, X-ray photoelectron spectroscopy, electrochemical impedance spectroscopy and X-ray absorption spectroscopy, respectively. As the results, the optimal ionic conductivity was achieved by the r.f. power of 75 W. Furthermore, the P-N valence states of hybrid orbitals were increased with increasing the nitrogen amounts.

Keywords: Lithium phosphorous oxynitride; X-ray photoelectron spectroscopy; X-ray absorption near edge structure; Electronic state; Ionic conductivity.

INTRODUCTION

Lithium phosphorus oxynitride (LiPON), a solid-state electrolyte, was first reported by Bates et al. from Oak Ridge National Laboratory (ORNL), USA in 1992. Owing to the following fascinating features: (a) an acceptable ionic conductivity of 3.3 × 10⁻⁶ S cm⁻¹ at room temperature, (b) a high electrical resistivity (larger than 10¹⁴ ohm cm), (c) a large electrochemical window voltage (up to 5.5 V vs. Li/Li⁺) at room temperature, (d) the absence of phase transformation over the wide temperature range, etc. LiPON has been regarded as not only a promising electrolyte but also a stable protective interphase film for all solid state rechargeable lithium battery.

In the past decade, LiPON has widely deposited via radio frequency (r.f.) magnetron sputtering, pulsed laser deposition (PLD), plasma-assisted directed vapor deposition (PA-DVD), ion beam-assisted deposition (IBAD). Among them, r.f. magnetron sputtering of lithium phosphate (Li₃PO₄) either in N₂ or a mixture of He/N₂ atmospheres is a favourable route due to the best morphology and ionic conductivity were available. During the sputtering procedure, bridging P-O-P and non-bridging P=O groups are partially replaced by incorporating the nitrogen atoms, resulting in formations of the doubly coordinated (P-N=P) (Nd) nitrogen and the triply coordinated (P–N< P) (Nt) nitrogen. However, it is found that ionic conductivity of LiPON was greatly depended upon the Nt ratio, which was attributed to more cross-linked networks were presented.

So far, influence of the sputtering parameters including r.f. power, N₂ pressure, bias, substrate temperature, and target to substrate distance on its ionic conductivity of LiPON thin film was extensively explored. To the best of our knowledge, electronic structure of LiPON correlated to the sputtering conditions has attracted less interest. X-ray absorption near edge structure (XANES) analysis using synchrotron radiation as X-ray source can provide a wealth of information on the local structure and electronic state. In this study, a series of LiPON thin films were first deposited by r.f. magnetron sputtering with various powers. X-ray diffraction (XRD) and scanning electron microscopy (SEM) were conducted to identify the crystal structure and make the morphological observation. Influence of r.f. power on the chemical environment, ionic

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conductivity and electronic state was further explored by X-ray photoelectron spectroscopy (XPS), electrochemical impedance spectroscopy (EIS) and XANES to investigate, respectively.

**EXPERIMENTAL**

**LiPON deposition**

LiPON thin films were deposited by r.f. magnetron sputtering (13.56 MHz) using a co-sputtering system (Kao Duen Technology Corp., Taiwan). The Pt/Ti/SiO₂/Si substrate was pre-cleaned by acetone and placed at a distance of 7 cm away from the Li₃PO₄ target (99.9%, 2 inch in diameter, Gredmann Ltd., Taiwan). The chamber was pumped to a base pressure of 4 × 10⁻⁶ Torr and then the Li₃PO₄ target was pre-sputtered for 10 min to remove any contaminating adatoms. The sputtering pressure was controlled at 13 mTorr using the N₂ atmosphere (99.999%), whereas the r.f. power was varied from 40 W to 120 W.

**Characterizations**

The crystal structure of each LiPON thin film was identified by X-ray diffraction (XRD) on PANalytical X’Pert Pro diffractometer (Cu Kα radiation, λ = 1.54 Å at 40 kV and 40 mA). The surface and cross-sectional morphologies were obtained using scanning electron microscope (SEM) on the Hitachi S-2400. N 1s spectra were collected by X-ray photoelectron spectroscopy (XPS, Al Kα radiation, λ = 8.34 Å, PHI Quantera). To evaluate its ionic conductivity, the electrochemical impedance spectra were measured by a frequency response analyser (FRA, Autolab PGSTA 20) from 1 MHz to 1 Hz. The O K-edge X-ray absorption near edge structure (XANES) of the LiPON thin film was recorded in the X-ray fluorescence-yield mode at the National Synchrotron Radiation Research Center (NSRRC), Taiwan. The energies of photons were calibrated with an accuracy of 0.1 eV employing the O K-edge absorption peak at 530.1 eV of CuO as the reference. Energy resolution of the monochromator was set at 0.22 eV for O K-edge X-ray absorption measurement. All XANES measurements were carried out at room temperature.

**RESULTS AND DISCUSSION**

**Structural identification and morphological observation**

A typical XRD pattern of the LiPON thin film deposited at 75 W was plotted in Fig. 1. Compared with the Li₃PO₄ (JCPDS 76-0556), no diffraction peak was detected, indicating that the as-deposited LiPON thin film was amorphous. This unique characteristic would be beneficial for the diffusions of lithium ions throughout the matrix. Fig. 2 showed the SEM images of the Pt/LiPON/Pt sandwich structure. Owing to its amorphous structure, no defects such as cracks and pinholes were observed from its top-view in Fig. 2 (a). Moreover, the cross-sectional view in Fig. 2 (b) revealed that the thin film was well adherent to the Pt surface and the interface also did not show any indication of defects.

**X-ray photoelectron spectroscopy (XPS) analysis**

To examine the influence of r.f. power on the chemical environment for each LiPON thin film, the as-deposited samples were characterized by XPS analysis, whereas the corresponding N 1s spectra were showed in Fig. 3. As indicated, the spectrum of each LiPON thin film can be resolved into two peaks, assigning to the doubly coordinated nitrogen (N_d) at 398.3 eV and triply coordinated nitrogen (N_t) at 399.6 eV, respectively. Percentages of N_d and N_t calculated from their respective areas of fitted peaks were further plotted as function of r.f. power in Fig. 4. It was noticed that the N_t % was raised from 35% to 62% as increasing the r.f. power from 40 W to 75 W. However, it was dramatically decreased to 27% while the applied power was
further increased to 120 W. When the r.f. power less than 75 W, the number and momentum of the ionized nitrogen (N+) were not enough to substitute oxygen atoms. For a given thickness (2.5 μm in the present study), it is anticipated that the sputtering time was decreased at elevated r.f. power. In other words, the possibility of N+ incorporated into the LiPON thin film was reduced. Accordingly, the Nt % was decreased when r.f. power was exceeded 75 W.

**Electrochemical impedance spectroscopy (EIS) measurement**

The Nyquist plots collected at room temperature were shown in Fig. 5 to evaluate the ionic conductivity of the LiPON thin films. The ionic conductivity was then calculated by following equation:

\[
\sigma = \frac{d}{(R \times A)}
\]

where \(d\) is the LiPON thickness, \(A\) is the contact area of metal, and \(R\) is the resistance determined from the measured impedance by selecting the \(Z\) value at the frequency at which \(-Z'\) goes through a local minimum. As expected, the ionic conductivity was decreased from \(4.2 \times 10^{-7}\) S cm\(^{-1}\) to \(1.6 \times 10^{-7}\) S cm\(^{-1}\) while the r.f. power was increased from 75 W to 120 W. This can be ascribed to high Nt percentage presented in the LiPON thin film, enhancing the mobility of lithium ions.

**X-ray absorption near edge spectroscopy (XANES) characterization**

To investigate the electronic structures of the LiPON thin films sputtered at various r.f. powers, the *ex situ* O K-edge XANES analysis was performed and the spectra subtracted the background were displayed in Fig. 6. The energy positions can be divided into three peaks: (1) A at 533.0 eV, (2) B at 534.9 eV and (3) C at 537.9 eV, respectively. It was found that peaks A and C were decreased.
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LiPON thin films with amorphous characteristic and no defects were observed from the XRD pattern and SEM images, respectively. XPS analysis revealed that maximum N\textsubscript{2} % was presented in the LiPON thin film deposited at 75 W. A high percentage of cross-linking N\textsubscript{2} in the structure was associated with greater ionic conductivity as determined by EIS measurement. On the other hand, O K-edge XANES spectra further demonstrated the peak intensity for the electronic transition from O 1s to P-N 2p\textsigma hybrid orbitals was increased while the nitrogen concentration in LiPON thin film was increased.

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