Short communication

Ion-implantation modification of lithium–phosphorus oxynitride thin-films

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Abstract

Among various solid electrolytes, the lithium–phosphorus oxynitride (Lipon) electrolyte synthesized by sputtering of Li_3PO_4 in pure N_2 has a good ionic conductivity of $2(\pm 1) \times 10^{-6}$ S cm^{-1} at 25 °C. As the nitrogen concentration increases in the Lipon electrolyte, the ionic conductivity is reported to increase as a result of a higher degree of cross-links. When Lipon films are deposited by sputtering, however, it is reported that the maximum nitrogen concentration saturates approximately at 6 at.%. By non-equilibrium processes, such as ion-implantation, nitrogen concentration can be controlled over 6 at.%. This study investigates the effect of nitrogen concentration on the ionic conductivity in Lipon films by using ion-implantation. Impedance measurements at 25 °C show that the nitrogen-implanted Lipon films enhance or retard the ionic conductivity over a wide range after nitrogen-implantation, when compared with as-deposited thin-films. © 2002 Elsevier Science B.V. All rights reserved.

1. Introduction

With the development of electronic devices, thin-film solid-state batteries have received greater attention for the fabrication of batteries that can be completely integrated with microcircuits, such as microdevices, microsensors, and very-large-scale integration (VLSI). The operational acceptability of such integrated devices is contingent on the high specific energy and low-power consumption of lithium-ion batteries [1–4]. Among all possible anode materials, lithium is the most attractive, since it has a favorable thermodynamic electrode potential with high specific capacity. Lithium metal, however, is very reactive with many solid-state electrolytes. Among various types of electrolytes, solid-sulfide electrolytes are excellent on account of their high ionic conductivity. Unfortunately, these materials typically form a resistive layer at the interface due to a reaction with

the lithium metal, and the performance of a lithium battery starts to degrade [5,6].

Lithium–phosphorus oxynitride (Lipon) thin-film was first developed by Bates et al. [7]. Lipon has a good ionic conductivity, viz., $2(\pm 1) \times 10^{-6}$ S cm^{-1} at 25 °C, and good electrochemical stability over 5 V(versus Li/Li$^+$). Bates et al. suggested that the ionic conductivity of Lipon is increased by the enhancement of cross-links due to nitrogen incorporation, and reported that the nitrogen amount in as-deposited Lipon is saturated at approximately 6 at.% [7,8]. In sputtering, nitrogen atoms substitute for bridging (–O–) or non-bridging (=O) oxygen atoms in Li_3PO_4. This leads to two-coordinated (–N=) or three-coordinated (–N$\langle$) nitrogen atoms, which cause higher cross-linked microstructures for increasing the ionic conductivity. Hence, it is considered that the ionic conductivity is closely related to the nitrogen concentration in Lipon. It was reported [7,8] that the typical composition of Lipon is $Li_{2.9}PO_{3.3}N_{0.46}$, which has a maximum nitrogen concentration of ∼6 at.%. There have been various attempts to increase the nitrogen concentration in oxynitride glass to incorporate more cross-links, but these
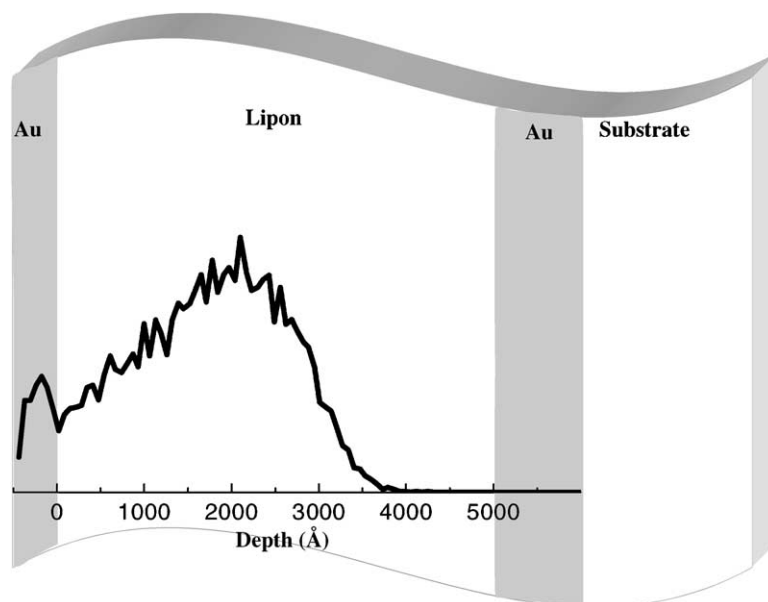
Fig. 1. Nitrogen profile in ion-implanted Lipon obtained by TRIM simulation.

have met with little success [9,10]. To date, the possibility of using ion-implantation for increasing the nitrogen content in Lipon has not been investigated. We expect that the ionic conductivity of Lipon will depend on several microstuctural factors, such as the nitrogen concentration, bonding configuration and structural relaxation in the amorphous thin-film [10,11]. In this article, the effect of excessive nitrogen introduced in Lipon by ion-implantation is reported.

2. Experimental procedure

The Li_3PO_4 target was fabricated from Li_3PO_4 powder (Kojundo, 99% up). Because β-Li_3PO_4 transforms to polymorphic γ-Li_3PO_4 at 520 °C, the target cracks easily [12]. Therefore, Li_3PO_4 powders were heated to 900 °C to prevent the Li_3PO_4 target from cracking before sintering. All targets were formed using powders cold-pressed into a disc-shaped mould, 2 in. in diameter, followed by sintering at 900 °C in a pure nitrogen atmosphere.

A RF magnetron sputtering system was used to deposit the Lipon electrolytes and the Au blocking electrodes. The Lipon electrolyte films were deposited at room temperature by sputtering in pure nitrogen (99.999%) at 10 mTorr with a flow of 10 sccm. The blocking electrodes, which were used to measure the ionic conductivity in Lipon, were made from gold which was sputtered in pure argon (99.999%) at 5 mTorr. For impedance measurements, an Au/Lipon/Au (500/5000/1000 Å/substrate) sandwich-cell structure was fabricated on a glass substrate with the area of 4 mm^2.

Rutherford backscattering spectroscopy (RBS) at oxygen resonance (3.076 MeV α particle) and nitrogen resonance
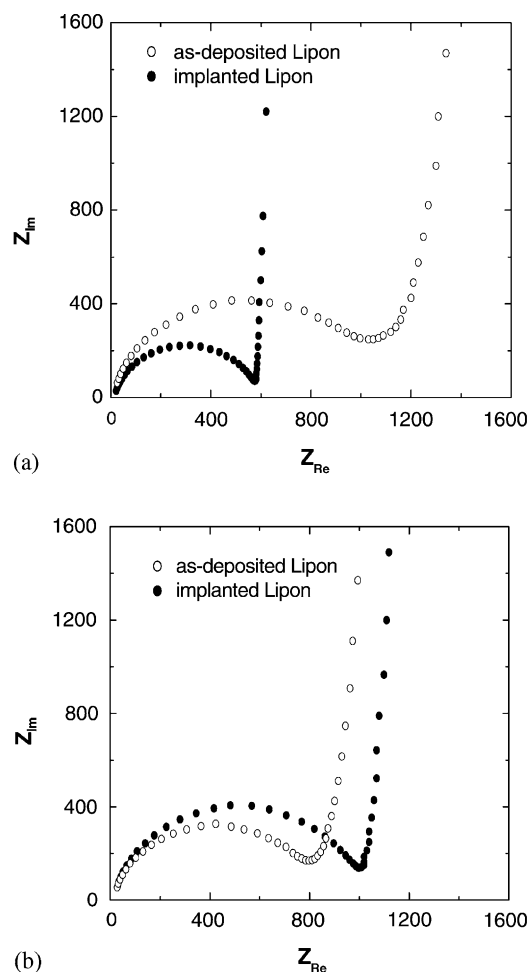

Fig. 2. Representative impedance spectra of ionic conductivity in 1.0 at.% excessive nitrogen-implanted Lipon: (a) enhanced case; (b) retarded case.

(3.694 MeV α particle) was used, with inductive coupled plasma (ICP) mass spectroscopy, to analyze the composition of Lipon films. The ion dose for nitrogen-implantation was determined from TRIM simulation [13]. Ion-implantation was performed on several cells of each batch. The thickness (500 Å) of the upper blocking electrode was chosen to minimize the ion-mixing effect at the interface [14]. The upper electrode was also useful for protecting Lipon from possible attack from moisture.

Impedance measurements for the ionic conductivity of Lipon were performed at room temperature. To make good electrical contact, copper wires were contacted to the gold electrodes. The impedance measurements were made in the frequency range from 50 Hz to 1 MHz with an ac impedance analyzer (IM6, Zhaner). The impedance was measured for several cells at each deposition batch, before ion-implantation (as-deposited) and after ion-implantation. The ionic conductivity σ, was calculated from $\sigma = (1/R) \times (d/A)$, where d and A are the Lipon thickness and the area of each cell, respectively. The ionic conductivity was determined from R by selecting the Z_{Re} value at the frequency at which Z_{Im} goes through a local minimum [7,8].

To analyze the change in microstructure between as-deposited and ion-implanted Lipon, Fourier transform infrared (FT-IR) spectra were measured from 1400–400 cm^{-1} for samples deposited on a double-sided polished Si(100) wafer. The spectra of Li_3PO_4, as-deposited Lipon, and nitrogen-implanted Lipon are compared.

3. Results and discussion

Lipon thin-films deposited by RF magnetron sputtering in pure nitrogen have an ionic conductivity of $1.35(\pm 0.3) \times 10^{-6}$ S cm^{-1} at 25 °C. The composition of as-deposited Lipon is $Li_{2.75}PO_{2.79}N_{0.58}$, as measured by RBS-resonance and ICP analysis. Although, the composition is different from that used by Bates et al. [7], viz., $Li_{2.9}PO_{3.3}N_{0.46}$, the ionic conductivity of the latter was quite similar at $2.3(\pm 0.7) \times 10^{-6}$ S cm^{-1}.
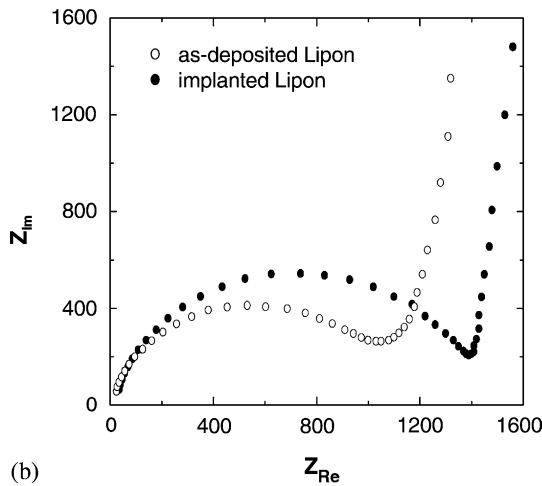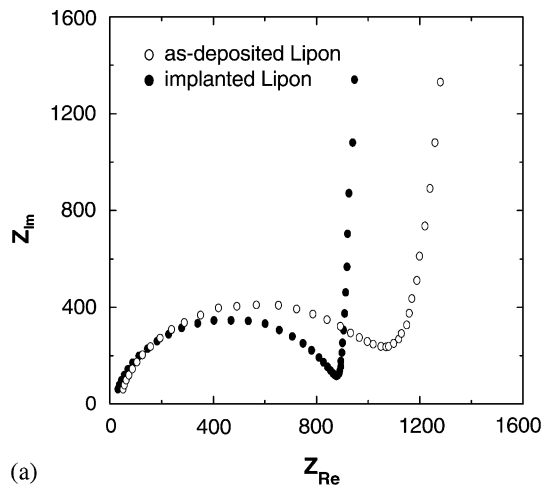

Fig. 3. Representative impedance spectra of ionic conductivity in 1.5 at.% excessive nitrogen-implanted Lipon: (a) enhanced case; (b) retarded case.
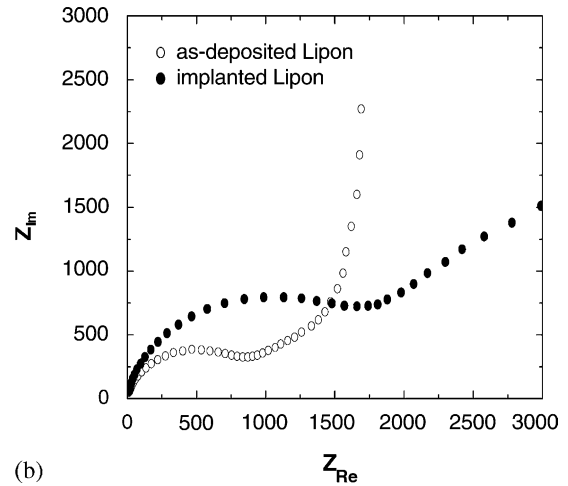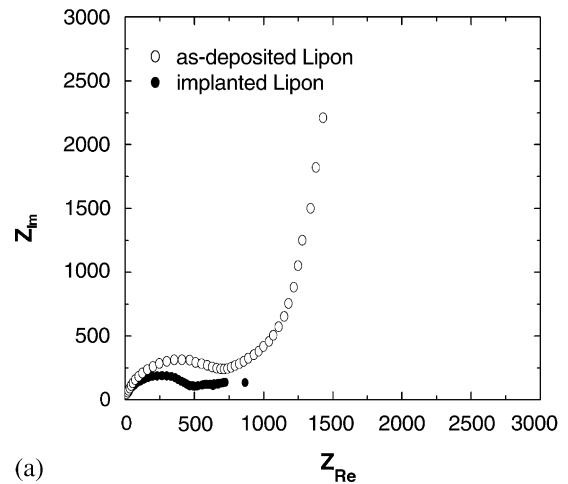

Fig. 4. Representative impedance spectra of ionic conductivity in 2.0 at.% excessive nitrogen-implanted Lipon: (a) enhanced case; (b) retarded case.
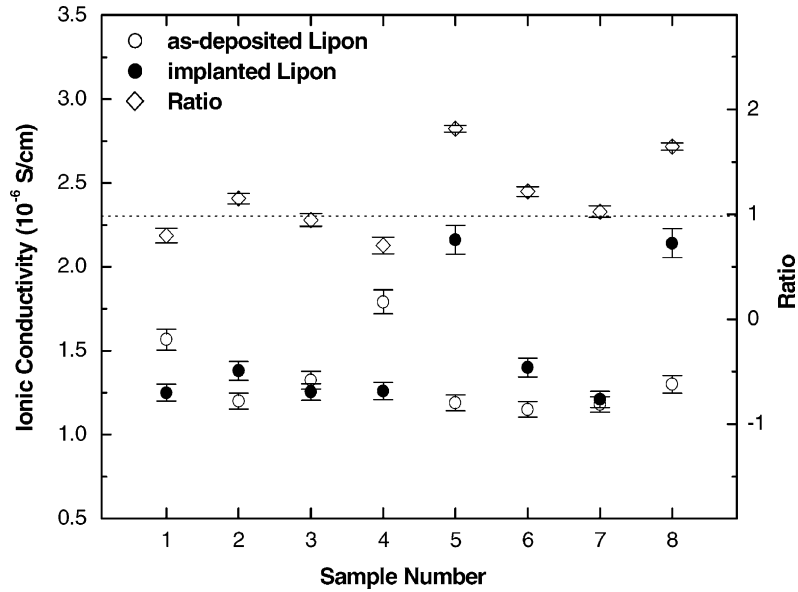
Fig. 5. Changes in ionic conductivity after 1.0 at.% excessive nitrogen-implantation for eight different samples.

To determine both ion dose and energy of nitrogen-implantation into Lipon, several different implantation parameters were tried by TRIM simulation in an Au/Lipon/Au sandwich cell (see in Fig. 1). As a result of the simulation, 1.0 at.% excessive implanted nitrogen was obtained by 2.06×10^{16} N cm^{-2} at 100 keV nitrogen ion. The ion doses for 1.5 and 2.0 at.%, excessive nitrogen were 3.09×10^{16} and 4.12×10^{16} N cm^{-2}, respectively.

The ionic conductivity was measured both before and after nitrogen-implantation for each Lipon cell. Representative impedance spectra are shown in Figs. 2–4 for the as-deposited and nitrogen-implanted Lipon. Among eight different samples with 1.0 at.% excessive nitrogen-implantation, the spectrum in Fig. 2(a) is for the material with enhanced conductivity, and that in Fig. 2(b) is for the material with the most retarded conductivity. As shown in Fig. 5, the changes in the ionic conductivity for eight different samples are not consistent. In the case of 1.5 and 2.0 at.% excessive nitrogen-implantation, the changes in ionic conductivity between as-deposited and nitrogen-implanted Lipon are similar to those for 1.0 at.% excessive nitrogen (Figs. 6 and 7). With excessive nitrogen content, it was originally expected that the ionic conductivity would be enhanced due to increasing cross-linked microstructures.
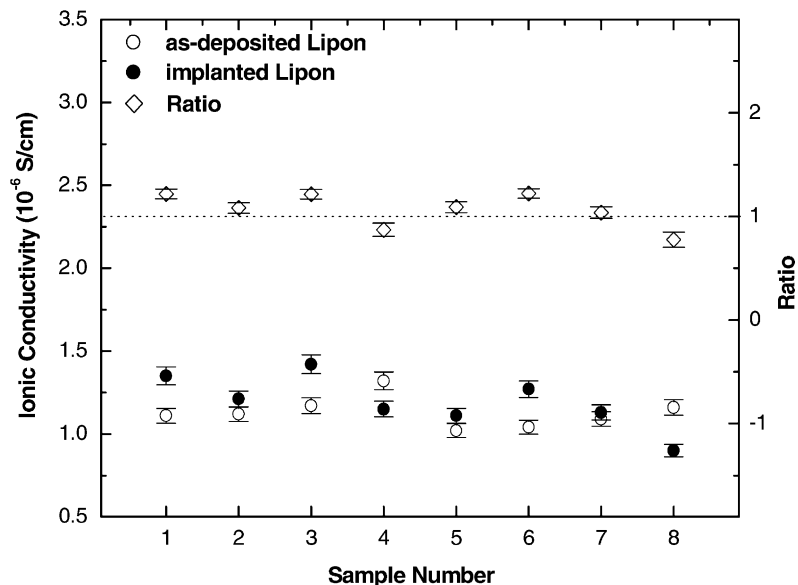

Fig. 6. Changes in ionic conductivity after 1.5 at.% excessive nitrogen-implantation for eight different samples.
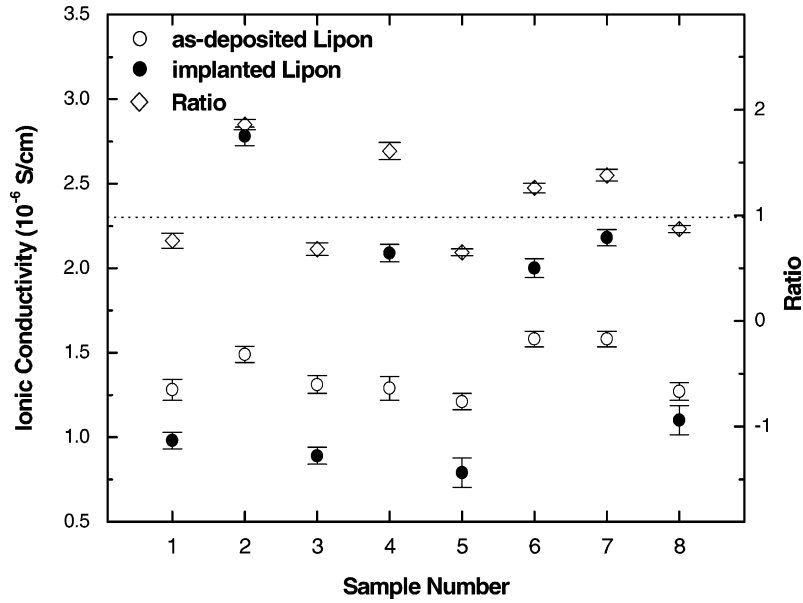
Fig. 7. Changes in ionic conductivity after 2.0 at.% excessive nitrogen-implantation for eight different samples.

Nitrogen-implanted Lipon, however, has not clearly shown such behaviour.

FT-IR spectra of Li_3PO_4, as-deposited Lipon, and nitrogen-implanted Lipon are given in Fig. 8. FT-IR failed to detect any potential differences in the microstructures of the as-deposited and ion-implanted Lipon. The FT-IR spectrum of a typical phosphate bulk glass, has four main transmission peaks which are ascribed to P=O (1280–1250 cm^{-1}), P–O$^-$ (1300–1100 cm^{-1}), P–O in the PO_3^{2-} (1000–990 cm^{-1}), and P–O–P groups (915–880 cm^{-1}) [15–17]. The FT-IR spectra of the Li_3PO_4 film also has four main peaks, at 1122, 1041, 925 and 582 cm^{-1} as shown in Fig. 8(a). The spectra of Li_3PO_4 films are found to be the same as phosphate bulk glass [15]. In the case of Lipon films, the FT-IR spect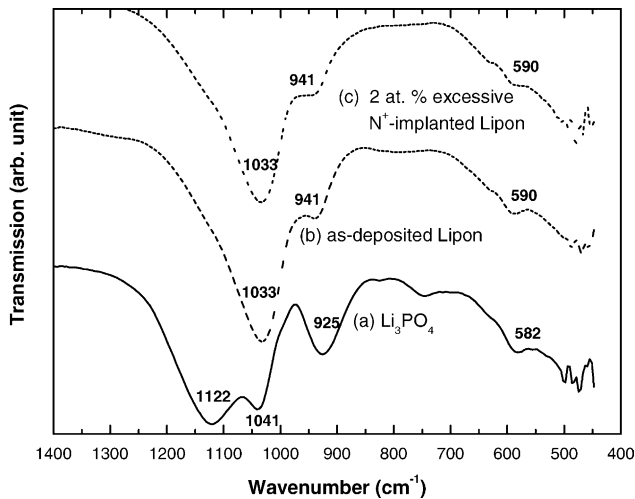ra are similar to Li_3PO_4 films, except that the peaks of the as-deposited Lipon are shifted to higher frequencies by nitrogen incorporation. This is because the nitrogen atoms substitute for oxygen in the as-deposited Lipon (Fig. 8(a), (b)). FT-IR spectra from the nitrogen-implanted Lipon appear very similar to the as-deposited Lipon. Further microstructural analysis is clearly needed for amorphous thin-films (with difficulty) to identify various atomic-scale microstructures, such as bonding configurations, structural relaxation, point defects, and bond-angle distributions. All these parameters may control Li-ion conduction in Lipon thin-films for enhancement or retardation.

4. Conclusions

Attempts have been made to modify the microstructures of as-deposited Lipon by nitrogen-implantation. The typical ionic conductivity of as-deposited Lipon is $1.35(\pm 0.03) \times 10^{-6}$ S cm^{-1} at 25 °C. To increase cross-linked microstructures in Lipon, nitrogen is incorporated into the as-deposited Lipon at 1.0, 1.5 and 2.0 at.% excessive nitrogen concentration. As a result of ion-implantation, the ionic conductivity of some samples is improved but of others is retarded. The FT-IR spectra display no distinct difference between the as-deposited and nitrogen-implanted Lipon. With excessive nitrogen incorporation in the as-deposited Lipon, no apparent trend in the change of ionic conductivity is found. While the relationship between ionic conductivity and atomic-scale microstructures in Lipon is complicated, we expect that the ionic conductivity of Lipon will depend on the nitrogen concentration, bonding configuration and structural relaxation in the amorphous thin-film. Therefore, mechanisms for the enhancement or retardation of ionic conductivity in Lipon after nitrogen-implantation need to be identified.

Fig. 8. FT-IR transmission spectra of various thin-films: (a) Li_3PO_4; (b) as-deposited Lipon, (c) 2 at.% excessive N$^+$-implanted Lipon.

Acknowledgements

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