Investigating the surface and interface of Li ion thin-film battery materials

Keywords
Li ion, LiPON, battery, GCIS, Argon cluster, energy storage

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Overview

There is a growing need to develop smaller more efficient energy storage materials to support the widespread use of portable electronic devices such as smart phones and tablets. The use of Lithium ion batteries was first proposed in 1973 with Li^+ ions acting as charge carries moving to the positive electrode during use and then changing direction during charging. The technology was commercialised in 1991 and has since superseded nickel hydride as the battery material for consumer electronics applications. More recently Li ion batteries are replacing lead-acid batteries for bulkier vehicle and aerospace applications.

Classical lithium ion batteries rely on a liquid electrolyte however there have been significant developments towards replacing liquid electrolytes with solid state thin-films. Thin-film lithium ion batteries offer improved performance by having a higher average output voltage, lighter weights thus higher energy density, and longer cycling life than typical liquid electrolyte batteries. In order to construct a thin film battery it is necessary to fabricate all the battery components, as an anode, a solid electrolyte, a cathode and current leads into multi-layered thin film. Lithium phosphorous oxynitride (LiPON) is widely used in solid state micro-batteries due to low electronic conductivity, increased durability to cycling and ease of preparation. Despite the widespread use of LiPON much is still unknown regarding Nitrogen bonding and Li mobility.

Here we will use conventional surface analysis techniques of XPS and sputter depth profiling to understand the surface and bulk chemistry of LiPON films formed via atomic-layer deposition (ALD). XPS yields quantitative information regarding the elemental composition of the near surface region to a depth of <10 nm. The elemental composition as a function of depth is probed and comparisons are made between the results obtained from conventional monatomic depth profiling and cluster depth profiling.

Experimental

All measurements were performed using the AXIS photoelectron spectrometer equipped with the gas-cluster ion source (GCIS). For these experiments the GCIS was run in high-energy cluster mode using 20 kV Ar_{1000}^+. High-energy cluster ions were used to enable depth profiling to be performed in a practical time frame. Sample rotation was used throughout the profiles to reduce the effects of sputter roughening and layer blending. LiPON thin-films were produced by ALD using Li precursors and a N_2 plasma [1]. LiPON films were previously characterized by optical ellipsometry to be ~50nm thick.

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Results and Discussion

After introduction into the analysis chamber a survey spectrum was acquired from the as-received sample. Analysis of the survey spectrum showed presence of the constituent elements Li, P, O and N and also a significant amount of carbon which can be attributed to the presence of adsorbed species from air exposure. To examine the distribution of Li throughout the film, depth profiling was performed. Figure 1 shows comparison of conventional monatomic depth profiling using 4 kV Ar^+ ions and the same sample profiled with 20 kV Ar_{1000}^+ ions. Both depth profiles were performed as an overnight experiment with the cluster mode etch rate >4nm/min.

There is a distinct difference between the two profiles. Under monatomic bombardment there is an initial increase in Li concentration after the first etch cycle – a consequence of removing surface contamination – then a subsequent decrease in Li into the bulk of the film reaching a steady-state of ~25.5 atomic%. Near the LiPON interface with Si substrate the Li concentration increases significantly reaching a maximum of 44%. By contrast when profiled 20 kV Ar_{1000}^+ ions the profile shows a different distribution of Li. An initial increase in Li concentration is shown after the first etch however there is no subsequent decrease reaching a steady-state of >31%. This amounts to an increase of 22% Li throughout the film depth compared to the monatomic profile. Interestingly no accumulation of Li was seen at the interface with the Si substrate. A comparison of the Li concentrations profiled using two different ions is shown in figure 2.

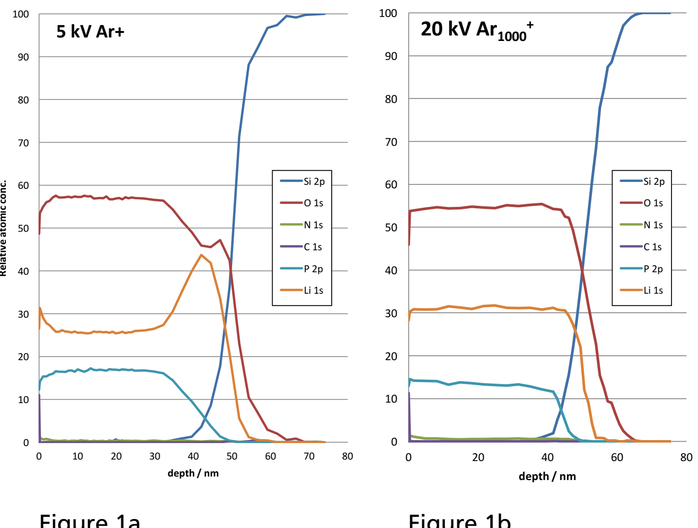

Figure 1a

Figure 1b

Figure 1: Depth profile of 50 nm LiPON thin-film using (a) 5 kV Ar^+ (b) 20 kV Ar_{1000}^+

Previously monatomic Ar^+ bombardment of glasses has shown lower than expected concentrations of light elements such as sodium [2]. This phenomenon was attributed to positive charge build-up in the near surface region from implanted Ar^+ ions. The charge build-up repels the small, mobile positive ions in the surface further into the bulk resulting in an underestimation in surface quantification. The same mechanism of Li ion repulsion and bulk migration is proposed to occur for LiPON thin-films analysed here. Li migration occurs under monatomic profiling resulting in an underestimation of Li concentration. Repulsive bulk migration also accounts for the increase in Li concentration at the interface with the Si substrate. The light ions are unable to penetrate through into the native Silicon oxide and instead accumulate at the interface. It must be noted that this system is particularly susceptible to this process because the Li+ ions in LiPON by their design are mobile for the charge transfer process.

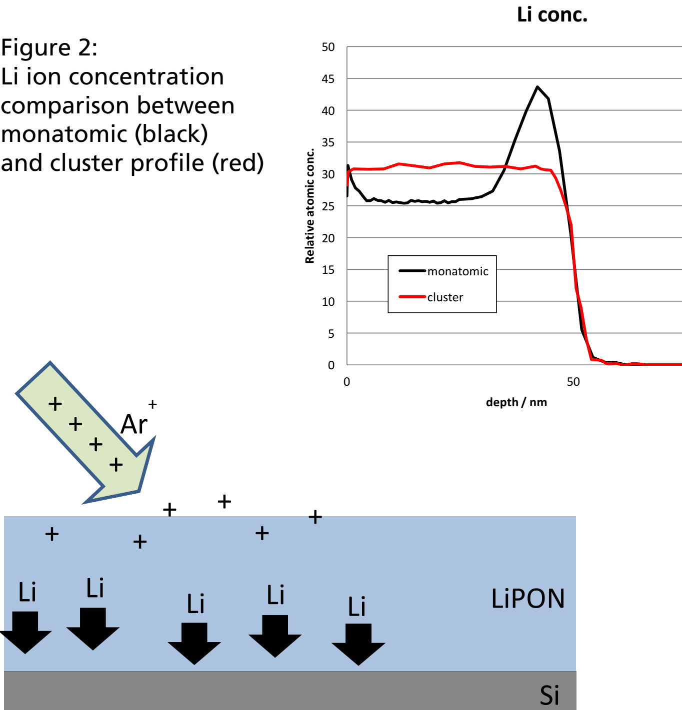

Figure 2:
Li ion concentration comparison between monatomic (black) and cluster profile (red)

Figure 3: Schematic of ion action on light elements.

Conclusion

It has been demonstrated that the use of XPS combined with depth profiling techniques provide quantitative information on the composition of LiPON thin-films created via ALD. It has been shown that the use of monatomic Ar^+ ions is unsuitable for profiling materials with mobile, light elements as the build-up of positive charge can cause migration leading to incorrect stoichiometry. It is concluded that the use of high energy Arn^+ clusters for depth profiling this class of materials is vital to mitigate the effects of ion migration and gain confidence in the validity of the results.

Acknowledgements

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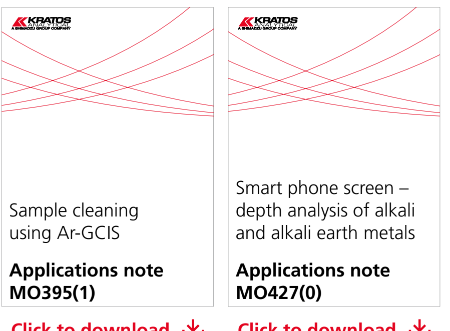

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