N_2/Ar flow ratio process on the structures and properties enhancement of LiPON film lithium cells

XIN JI [*], LIN JUN WANG, YI MING MI[a], CHAO MIN ZHANG[a]
School of Materials Science & Engineering, Shanghai University, Shanghai 200444, China
[a]*College of Fundamental Studies, Shanghai University of Engineering Science, Shanghai 201620, China*

Sputtering deposited LiPON films are of potential important as solid electrolyte layer in thin-film lithium cells as long as we can optimize the flow ratio process to enhance their electrical and electrochemical properties. The aim of the present study is to find the structural transformation mechanism and predict the enhanced electrochemical properties of LiPON films as a result of flow ratio processes. The results show that high flow ratio processes not exceeding 0.3 can produce regrown and agglomerate of the LiPON amorphous structure by an activated growth mechanism. In addition, an inverse relation between the flow ratio process and carrier mobility is observed in the enhancement of the electrical properties of the LiPON films. Finally, high flow ratio processes are found to be vital for the increase of the transmission rate of lithium ion which can be beneficial to enhance the efficiency of LiPON lithium cells.

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Li-ion conducting and solid electrolyte films have attracted much attention in their application to lithium thin film cells [1, 2]. The lithium thin film cell is fabricated by anode, cathode and electrolyte layers. Among the electrolyte materials the LiPON is an ideal solid electrolyte which possesses many attractive properties such as high ionic conductivity, low electronic conductivity, good thermal stability and resistance to dielectronic breakdown [3, 4]. Therefore, LiPON films have an important role in designing the electrolyte layer by selecting appropriate constituents. The structural parameters of the LiPON films are responsible for the efficiency of lithium cell devices. Hence, an accurate knowledge of structural properties is very important [5, 6]. Therefore, studying the structures of semiconductor materials not only reveals the physical and electronic properties of semiconductors, but their vital role in high efficiency electronic devices.

Many theoretical and experimental works previously have been interested with the structural and electrochemical properties of LiPON films. The sputtering method is the most popular metal transformation process for producing complex compounds [7, 8], since it is capable of producing different components, and also because of its great economic advantages and high production rates. In fact, many research efforts have been directed at developing sputtering parameters with the aim of forming LiPON films with better properties [9, 10].

Over the last few years, various authors have studied the sputter deposited process used for energy materials [11, 12]. Among these processes flow ratio can be developed as a cost effective approach. In this technique, the main aspect studied has been on the effect of the flow ratio process on synthesis and surface characteristics during the deposition cycle [13, 14]. However, this directly affects the structural changes when one layer is linked to another. None of the previous reports mentions this latter aspect, and no one considers the possibility of improving the electrochemical properties [15, 16]. There are also no references to these kinds of studies when the films are used in lithium cells. In this article, the flow ratio process is designed to speed up the structural transformation of LiPON films, in order to find a useful method for the manufacture of highly effective LiPON film lithium cells [17, 18].

In this work, LiPON thin films are deposited at radiofrequency reaction sputtering using a magnetron sputtering system. The effects of flow ratio process on the structural and electrical properties of LiPON thin films are investigated systematically using atomic force microscopy and electrochemical measurements. The results obtained and related discussions are useful as indications for the potential applications of LiPON films.

1. Experiment

1.1 Synthesis of LiPON thin films

Solid lithium cells were fabricated with the structure SFO/ LiPON/Cu. A LiPON buffer layer was deposited first on an SFO (SnO_2: F) glass electrode layer using 50 W power, and then the Cu electrode layer was deposited at 100 W power on the LiPON solid electrolyte layer.

Thin films of Cu was deposited by direct current sputtering and that of LiPON was by deposited by radiofrequency reaction sputtering using a magnetron sputtering system (FJL560D2). Cylindrical Li_3PO_4 and Cu ceramic targets of 8 cm in diameter were used. No changes in target composition were observed with time and usage. The deposition chamber's base pressure was 1.6×10^{-4} Pa, and during the deposition of Cu electrode layer, the gas pressures were maintained constant at 0.5 Pa. The substrate-to-target distance was 100 mm. Depositions of Li_3PO_4 and Cu layers were performed at room temperature for 120 and 30 min, respectively. Finally, during the deposition of Li_3PO_4, the Ar gas pressure was 1.0Pa and the flow ratio ratios (N_2/Ar) were held on 0.3, 0.5, 1.0, 2.0 and 3.0.

1.2 Characterizations of LiPON films

To investigate the crystallographic properties of the films, coupled θ–2θ X-ray diffraction (XRD) scans were performed in the range 2θ = 20–80° by use of the Cu $K_{\alpha 1}$ line of an X-ray source (Rigaku D/max2550). The surface morphologies of films were examined by atomic force microscopy (DI Nanoscope IIIA Multimode). The resistivity calculated from the sheet resistance measured by a four-piont probe. All the electrochemical experiments were carried out with Mac Pile II system (Bio-Logic) in a dry atmosphere at a dew point of less than 25^{o}C.

2. Results and discussion

2.1 Effects of flow ratio processes on structural transformation

It is seen from Fig. 1 that the film prepared by reaction sputtering process shows six strong diffraction peaks of the orthorhombic phase. These peaks can be indexed to (021), (220), (131), (222), (331) and (260) Li_3PO_4 crystal planes, respectively. On the basis of orthorhombic structure, the film is in good agreement with the data of orthorhombic Li_3PO_4 polycrystalline structure. In addition, no obvious diffraction peak just a wider package is observed around 25°, which indicates the existence of LiPON amorphous structure. It reveals that using sputtering technology can transform the Li_3PO_4 crystalline structure into LiPON amorphous structure in room temperature and N_2 atmosphere.

Similarly, the preferential orientation of the Li_3PO_4 planes in the films became much stronger with the increase of gas ratio, which indicates that Li_3PO_4 particles of better crystallinity and larger grain size are formed, which indicates the growth of LiPON amorphous structure.

Obviously, the high N_2 pressure process contributes to the diffusion of atoms adsorbed on the substrate and accelerates the migration of atoms to energetically favourable positions, resulting in an increase of the LiPON grains. It is also reasonable to assume that high gas ratio process not exceeding 3.0 can produce a highly effective LiPON thium cell which contains the LiPON amorphous structure in the solid electrolyte layer.

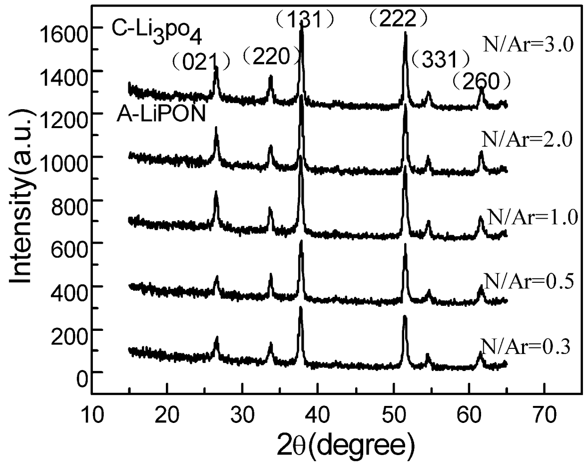

Fig. 1. XRD patterns of LiPON films prepared at various flow ratios.

2.2 Effects of flow ratio processes on grain growth

Fig. 2(a)-(e) shows the atomic force microscopy surface morphologies of LiPON films deposited at flow ratios of 0.3, 0.5, 1.0, 2.0 and 3.0, respectively. It is found that the flow ratio process has a great influence on grain nucleation and growth. At the flow ratio of 0.3, the grain size is smaller and the crystal quality is poor. With the increase in flow ratio from 0.3 to 0.5, larger-sized grains and better-crystallized films are obtained, which is due to the relatively high mobility of the particles on the substrate surface at higher flow ratio. The LiPON films deposited at the flow ratio of 0.5 has an average grain size of 4.9 nm. The interface of the grains can be seen clearly at the flow ratio of 0.5; while, as shown in Fig. 2(C), when the flow ratio is increased to 1.0, the interface of the grains becomes not that clear and the sintering of grains occurs.

Obviously, as presented in Fig. 2(d) and (e), LiPON films with larger grains are gained, 6.0 nm for LiPON at 2.0 and 7.0 nm for LiPON at 3.0. The cracks between grains are easily to be observed. Crack-free and compact LiPON films can be attained at the high flow ratio. To fabricate high efficiency LiPON lithium cells, LiPON with larger grains are needed. Therefore, the relatively high flow ratio process is contributed to deposit LiPON lithium cells. In addition, the films deposited at the flow ratio of 2.0 and 3.0 exhibit a columnar structure and the surfaces become rougher, which shows that it is easy for the grains to agglomerate with each other through an activated growth mechanism during the deposition at the high flow ratio.

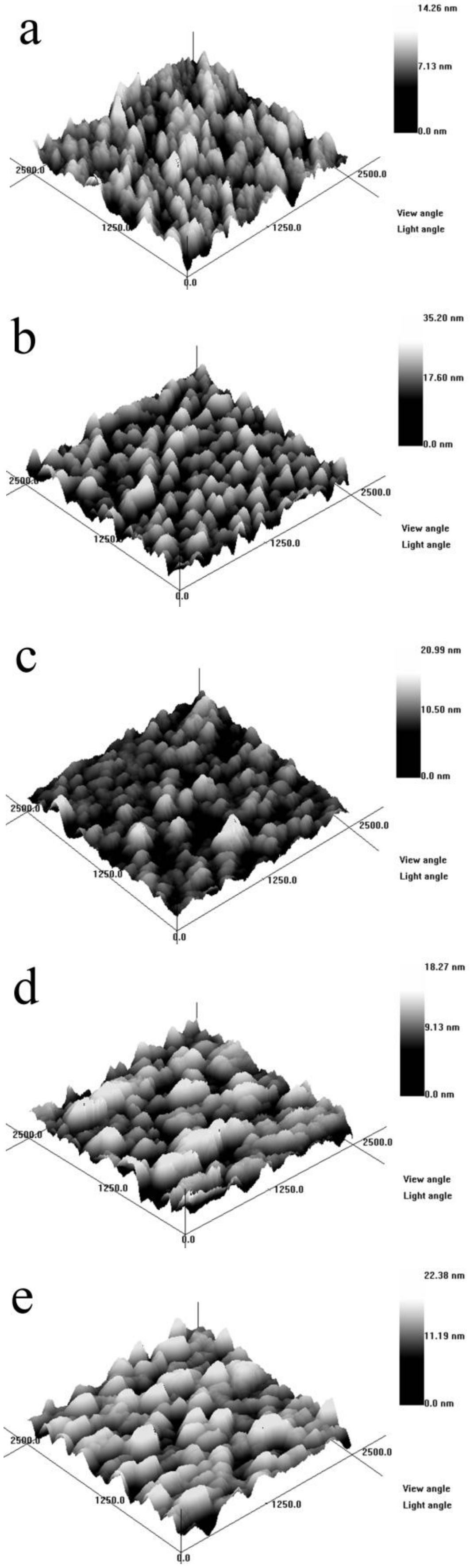

Fig. 2. AFM images of LiPON films prepared at various flow ratios: (a) 0.3; (b) 0.5; (c) 1.0; (d) 2.0; (e) 3.0.

2.3 Effects of flow ratio processes on electrical properties

Fig. 3 illustrates the resistivity calculated from the sheet resistance measured by a four-point probe for LiPON films at different flow ratios. It is found that LiPON films prepared at higher flow ratio exhibit the lower resistivity, therefore suggests that the conductivity of these films are higher. One of the reasons for such a behavior may be due to the presence of well-grown grains in such films. On the other side, defects apparently tend to segregate out of the LiPON grains more rapidly.

Moreover, it also can be seen in Fig.3 that the film (0.3) shows the higher resistivity (5.5Ω.cm) than other films at high flow ratios. The reduction of the electrical properties of the films at the higher flow ratio is associated with number of cavities and large-angle grain boundaries, which will increase charge carrier scattering and result in decrease of carrier mobility.

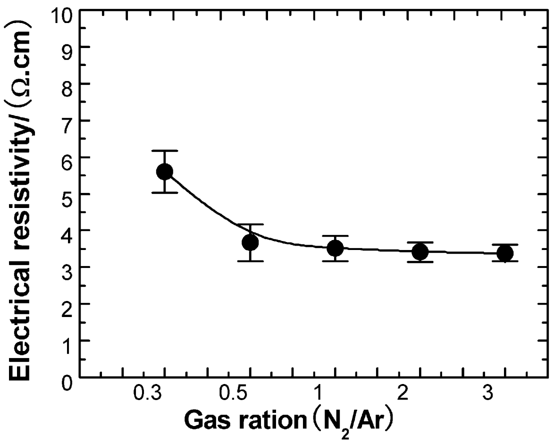

Fig. 3. The resistivity of LiPON films deposited with different flow ratios

2.4 Effects of flow ratio processes on electro chemical properties

Fig. 4 shows the discharge curves of all-solid-state thin-film lithium battery at various current densities. It can be seen in Fig. 4 that the discharge capacity of the LiPON films increases with increasing flow ratio processes. Evidently, the LiPON battery at high flow ratio process (3.0) exhibits the highest discharge capacity of about 24 mAh cm^{-2}.

The significant increase in the discharge rate implies that high flow ratio process has a more obvious effect on the reduction of lithium ions number available for deintercalation, which leads to a depletion over potential at the electrode surface due to mass transport. Therefore, the higher state of charge and lower discharge rate is a good way to enhance the discharge efficiency of LiPON film lithium cell.

In addition, it can also be observed that the high flow ratio process can reduce the interfacial impedance between particles and increase the transmission rate of lithium ion. In this result, the big sized grain with amorphous structure at the high flow ratio is beneficial to the conduction of Li ion.

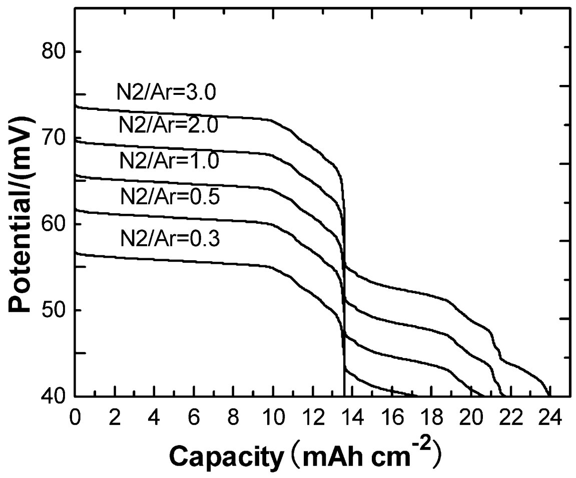

Fig. 4. Plot of $(h\upsilon)^2$ versus hυ for the LiPON films prepared at various flow ratios.

3. Conclusions

In conclusion, we systematically investigated the structural transformation and electrochemical properties of LiPON films at different flow ratio processes. This indicates that all flow ratio processes not exceeding 3.0 can produce LiPON amorphous structure. Also, the high flow ratio process can contribute to an increase of the LiPON grains. In addition, high flow ratio processes have a strong effect on the growth and agglomerate of the LiPON amorphous structure by an activated growth mechanism. Finally, we find that high flow ratio processes can cause a significant increase in the transmission rate of lithium ion, which can be beneficial to enhance the efficiency of LiPON lithium cells.

Acknowledgements

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*Corresponding author: jixin@sues.edu.cn