

A study of electronic shorting in IBDA-deposited Lipon films

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Abstract

Because a near term goal of our research is to obtain optimal performance LiCoO₂/lithium phosphorus oxynitride (Lipon)/C thin film batteries, and due to the major importance of the electrolyte in any battery, we have recently been attempting to better understand the causes of electronic shorting in our Lipon electrolyte films. After studying the residual and temperature-dependent stress of these films and observing cracking after they had undergone a temperature change from 300°C to room temperature, we adopted a model in which the thermal expansion coefficient mismatch between Lipon and our glass substrates accounted for the cracking and therefore led to the shorting. This model was also supported by evidence that Al films (which had thermal expansion coefficients close to that of Lipon and proved to act as “buffer layers” by preventing cracking of Lipon when glass/Al/Lipon structures were cooled from 300°C to room temperature) were successfully used to produce short-free Al/Lipon/Al devices. © 2000 Elsevier Science S.A. All rights reserved.

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1. Introduction

For the past several years, lithium phosphorus oxynitride (Lipon) has been used as a solid state electrolyte for lithium batteries [1,2]. A large stability window vs. Li metal (from 0 to 5.5 volts [2]) and a relatively high ion conductivity (2×10^{-6} S cm⁻¹ [2] at room temperature) are among the features that make it especially valuable for this use. While rf magnetron sputtering of Li₃PO₄ in either N₂ or He + N₂ atmospheres has been the common method used to deposit Lipon (Refs. [1,2] and also by our group in the past), recently we have been studying a deposition process, termed ion beam directed assembly (IBDA), for controllably and rapidly ($> 5 \text{ \AA/s}$)¹ depositing these films [3]. To date, the properties of our IBDA-deposited Lipon compare favorably with our rf sputter-deposited Lipon. This includes its having higher: (a) mass density ($\geq 2.4 \text{ g/cm}^3$ vs. $\leq 2.0 \text{ g/cm}^3$ for rf sputter-deposited Lipon); (b) lithium ion conductivity (1.5×10^{-6} S/cm vs. 5×10^{-7} for rf sputter-deposited Lipon); and (c) decomposition voltage ($> 6 \text{ V}$ vs. 5.5 V for rf sputter-deposited

Lipon). However, electronic shorts have been encountered repeatedly in our devices. This challenging problem, which prevents accurately studying IBDA-deposited electrodes (e.g. C and LiCoO₂) of our thin film solid state lithium battery, motivated us to investigate further some of the thermomechanical properties of IBDA-deposited Lipon films, since their cracking due to thermal stress was suspected to be the principal cause of the shorting.

2. Electronic shorts study

2.1. Experimental

Since we started producing IBDA-deposited Lipon films, (metal/electrolyte(Lipon)/metal) devices (MEMs), in which the metal was either Pt or Al, were routinely used to evaluate the electrical properties of the Lipon films.

The Lipon films in this study were IBDA-deposited by thermally evaporating Li₃PO₄ using a resistance heated tungsten boat and simultaneously bombarding the substrates with nitrogen ions provided by a Commonwealth Scientific Mark I ion gun. The substrates (Corning # 2947 glass) were mounted on a planetary system so that they were spun and rotated around the chamber, which ensured a homogeneous thickness. The basic parameters of the Lipon depositions were: base pressure using an oil-diffu-

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¹ The deposition rate is primarily limited by the nitrogen ion beam current density, and this can be increased by utilizing more and/or higher anode current ion guns.

sion pump $< 10^{-6}$ Torr, nitrogen flow rate ≈ 9.8 sccm, chamber nitrogen pressure $\approx 2 \times 10^{-4}$ Torr, Commonwealth Scientific Mark I ion gun anode voltage ≈ 90 V and anode current ≈ 0.9 A, deposition rate > 5 Å/s. The films were deposited intermittently to keep the samples from heating too much due to radiation from a tungsten boat from which the Li_3PO_4 was evaporated as well as radiation from the filament of the ion gun. A Chromel–Alumel thermocouple embedded in a carbon block was used to monitor the temperature. The reading for that thermocouple was considered to be the highest attainable temperature for the samples and was kept under 100°C during these depositions. Under this constraint, each partial deposition lasted about 4–5 min and the system was allowed to cool down for at least 2 h between partial depositions.

The platinum films for the MEM structures were deposited by rf sputtering (100 W, 5-in. diam. target, base pressure $< 10^{-6}$ Torr, 10 mTorr argon = process gas); and the aluminum films were deposited by electron beam thermal evaporation (base pressure $< 10^{-6}$ Torr, deposition rate > 1 nm/s). In none of these depositions, including that of Lipon, were the substrates intentionally heated.

The MEM sandwiches that we fabricated for this study were deposited under the previously mentioned conditions onto 25×75 mm², 1 mm thick microscope slides. The metal electrodes were deposited through metal masks, resulting in a crossed grid configuration. By using three 3-mm wide, 75-mm long strips as the bottom contacts and eleven 3-mm wide by 25-mm long strips as the top contacts 33 MEM cells (each one with an active area of 9 mm²) were obtained for each sample. In the Al/Lipon/Al samples the Al contacts were approximately 1200 Å thick, whereas the thickness of the Pt contacts was approximately 1400 Å. The Lipon was deposited over the full area of each sample.

These sandwich structures were used to determine the presence of electronic shorts in our Lipon. Cells were considered to be electrically shorted when a steady (non-decaying) current across them was measured after applying a step voltage. A Model 362 PAR potentiostat was used for this purpose.

After studying the yields (defined as the fraction of MEMs that were not shorted after the deposition), the same samples were heated to 300°C on a hot plate in the laboratory atmosphere and cooled by removing the samples from the hot plate and placing them on a room temperature metal plate. With the model of cracks due to thermal stress in mind, this experiment was carried out to see whether or not cracking occurred upon thermal transients of the films and to study the effect of the metal underlayers.

A measure of the relative expansion coefficients of our Lipon, Pt and Al films with respect to glass was obtained by measuring the temperature dependence of the stress using the apparatus described by Aoki et al. [4]. The

technique consists of applying two parallel laser beams to the film and using the measured deflection of the reflected beams relative to each other to calculate the radius of curvature of the sample. With that piece of information and the Stoney equation (cf. Eqs. (9)–(13) in Ref. [5]) one can determine the stress of the film at a given temperature. A resistance heater (imbedded in an aluminum block on to which the samples were mounted) was used to control the temperature, which was monitored with a Chromel–Alumel thermocouple. The samples were generally heated to a maximum of 110°C . For this experiment, 2300-Å-thick Al films were deposited on two 25×25 mm² cover glass slides (approximately 0.150 mm thick) under the same deposition conditions that were described previously for the Al/Lipon/Al structures. Approximately 220-Å-thick Pt films, sputtered also under the previously mentioned conditions, were deposited on four cover glass slides. The temperature dependent change in the curvature of the sample, and therefore the temperature dependent change in stress, was measured along two perpendicular directions in the plane of the slide for each sample. Thus, we had four sets of data for the change of stress as a function of temperature for the Al films and eight sets for the Pt films.

Both the residual stress and the temperature dependence of the stress in 25 of the IBDA-deposited Lipon films were also measured using the above described apparatus [4].

3. Results and discussion

From the yields study we found that 27% (9 out of 33) of the platinum MEM cells had electronic shorts, whereas 0% (none out of 33) of the aluminum MEM cells had shorts. This was consistent with earlier observations where MEMs with Al were always found to provide better yields than MEMs with Pt.

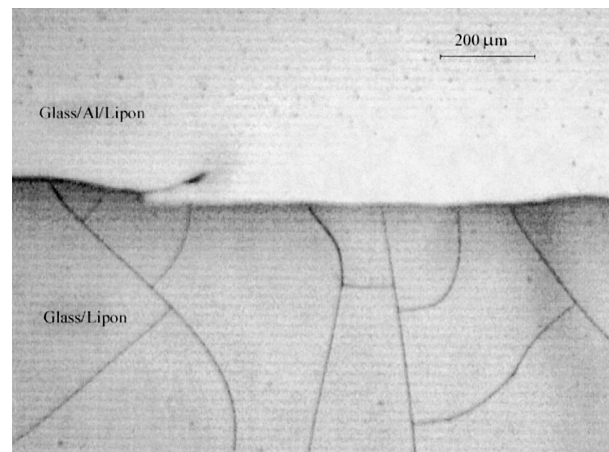


Fig. 1. Photograph of cracks in Lipon after heating up to 300°C and subsequently cooling the sample to 23°C . Cracks stop at the region where there is an aluminum film between the substrate and the Lipon film.

After the MEM samples were heated on the hot plate and allowed to cool down to room temperature, cracking was observed in Lipon. Interestingly, cracking in the Lipon showed differences depending on the nature of the metals that we used as under-contacts. While in both samples cracking occurred where the Lipon film was covering the otherwise bare glass substrate, for the Al/Lipon/Al sample the cracking ended abruptly wherever an Al strip was underneath the Lipon film (cf. Fig. 1). In the case of the Pt/Lipon/Pt sample, however, not only did the cracking not end at the Pt underlayers, but (even as observed by eye using grazing incidence illumination) the density of cracks in those regions where the Lipon covered the Pt strips was higher than in those regions where the Lipon covered bare glass and the cracks even had a different appearance (cf. Fig. 2). On the other hand, the top contacts on either of those two MEM samples did not alter the arrangement or location of the cracks.

For each data set of change of stress vs. increment of temperature a linear fit was carried out. The average slope of four sets of data of the Al films was -12×10^5 Pa/°C, with a standard deviation of 1×10^5 Pa/°C. These samples always returned to their initial room temperature stress conditions after being heated. For the Pt samples the average slope was $+2 \times 10^5$ Pa/°C with a standard deviation of 3×10^5 Pa/°C. In this case the samples did not always return to their initial stress conditions. Even though the change in stress of the Pt films was more unpredictable (as indicated by the relatively large standard deviation compared to the average slope), perhaps due to an inhomogeneity in their thickness, the magnitude of the average slope was one sixth of that for Al films. Since the slope of

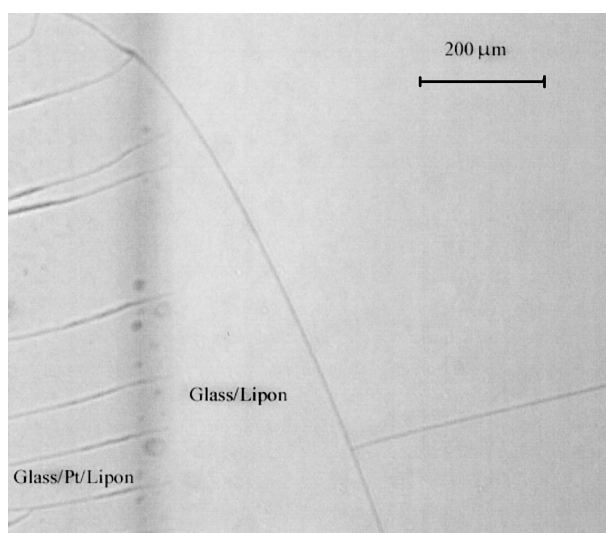


Fig. 2. Photograph of cracks on an MEM device with Pt contacts. Cracks formed everywhere upon heating up to 300°C and subsequently cooling the sample to 23°C. The density of cracks was larger in the areas with Pt strips under the Lipon than in areas with Lipon in direct contact with the glass substrate.

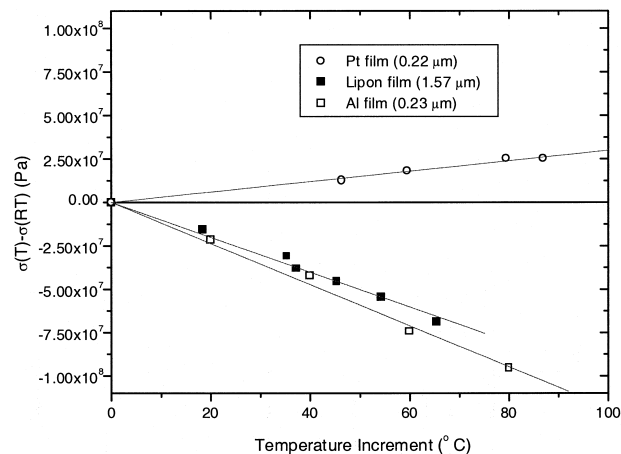


Fig. 3. Representative sets of data of change of stress vs. temperature increment (initial temperature = 23°C) for Pt, Al and Lipon films. The slope ($d\sigma/dT$) is proportional to the difference in thermal expansion coefficients of the films and the cover glass [5]. Namely, the thermal expansion coefficients of Lipon and Al are larger than that of the cover glass, while that of Pt is smaller for that particular film.

the change in stress vs. increment of temperature is proportional to the difference of thermal expansion coefficient of the film and the substrate Ref. [5]), these findings suggest that the thermal expansion coefficient of our Pt films was either comparable to that of glass or slightly smaller, whereas the thermal expansion coefficient of our Al films was clearly larger than the glass. This compares well with the tabulated data for the thermal expansion coefficients of Al ($25 \times 10^{-6}/^{\circ}\text{C}$ at 25°C [6]), soda lime glass produced by Corning ($9.35 \times 10^{-6}/^{\circ}\text{C}$ in the range 0–300°C [7]) and Pt ($9 \times 10^{-6}/^{\circ}\text{C}$ at 25°C [6]).

The residual stress of our IBDA-deposited Lipon films has consistently been found to be tensile, ranging from 6×10^7 to 3.2×10^8 Pa for different deposition parameters,² and always became less tensile, also consistently, for depositions at elevated temperatures. The slopes of the change in stress vs. temperature increment for the IBDA-deposited Lipon films ranged from -5×10^5 Pa/°C to -13×10^5 Pa/°C, also for different deposition parameters. Three representative data sets of change of stress vs. increment of temperature for the three types of films that we studied are shown in Fig. 3.

The latter two observations mentioned regarding stress in our Lipon films, together with additional observations that the higher the temperature the chamber reached during

² This includes different anode voltages of the ion gun (between 80 and 150 V), different anode currents (between 0.53 and 0.99 A), different deposition rates (between 2.5 and 6.1 Å/s) and both intermittent and continuous depositions. Even though this earlier work was not part of this current study, it was observed that there existed a correlation between continuous depositions (in which case the substrates reached higher temperatures than reported here) and higher residual stresses in the films after the deposition.

the Lipon deposition, the larger the residual stress in the films, and that cracking was observed after heating and cooling the samples on a hot plate, led us to conclude that: (a) the thermal expansion coefficient mismatch between the Lipon films and our glass substrates (the coefficient of Lipon being greater than that of glass) is the main source of stress in the films, and (b) the thermal mismatch can account for the cracking that occurred upon cooling in Lipon films which were part of any MEM samples that were heated to approximately 300°C on the hot plate.

The observations made of samples after they were heated and cooled on a hot plate show clearly that our Al films prevented the cracking of Lipon whereas our Pt films did not, or, if anything, the Pt films enhanced the cracking. A hand-waving argument that can be given to explain this behavior, just by taking into account the relative thermal expansion coefficients of our Pt, Al and Lipon films with respect to glass, is as follows. Upon cool-down, cracking occurs because, given their relative expansion coefficients, Lipon tends to shrink more than the glass substrate, (which is much thicker than the Lipon film and therefore restrains the Lipon), resulting in the Lipon being under high tensile stress that can be relieved only by cracking. If we regard the glass/Al/Lipon structure as a Lipon film deposited on a glass/Al substrate, the upper atomic layers of the Al will shrink upon cool-down more than the glass and therefore will relieve the stress on the Lipon film. That is, the aluminum film acts as a “mechanical buffer” between Lipon and the glass substrate. On the other hand, for the glass/Pt structure the upper atomic layers of the platinum will resist shrinking as much as the bare glass, if not less so, leading to a state of high stress on the Lipon film similar or larger than that caused by the bare glass alone.

Finally, the fact that there is a correlation between the inhibition or enhancement of cracking by the two kinds of metal contacts that we studied, together with the incidence of shortings observed in the MEM structures, suggests that electrical shorts can be caused by cracking of the Lipon upon cooling following the Lipon deposition itself. (It should be noted that the temperature during the IBDA deposition of Lipon builds up in the chamber due to radiation from a tungsten boat from which the Li_3PO_4 was evaporated as well as from the filament of the ion gun.) The shorting then occurs during any of the next depositions, which are electronically conductive films.

4. Conclusions

The above study of some of the thermomechanical properties of films of two metals (Pt and Al) that were being used as contacts to evaluate our IBDA-deposited Lipon and as current collectors in our thin film batteries, indicates that there exists a strong correlation between: (a)

their relative thermal expansion coefficients with respect to Lipon and our cover glass substrates; (b) whether or not the metal films prevent cracking when the MEM structures undergo a relatively large thermal transient; and (c) the yields that were observed in MEM structures that incorporated these metals. That is, our Al films, which appeared to have a thermal expansion coefficient similar to that of Lipon (and the thermal expansion coefficient of both were greater than that of cover glass), also prevented cracking of Lipon when deposited between Lipon and the glass substrate and thereby provided good yields for MEM structures. According to our thermal expansion model for explaining the cracking of Lipon, our Al films alleviated the state of high stress in our Lipon films and therefore prevented their cracking and shorting. On the other hand the use of sputter-deposited Pt films, whose thermal expansion coefficients seems to be similar to or smaller than that of cover glass and thus did not inhibit cracking in Lipon, resulted in much poorer yields when used in MEM structures.

These experimental results suggest that electrical shorting might be overcome if the correct metal (and perhaps thickness) is chosen for the current collectors for thin film batteries. We are currently studying what the optimal thickness of an Al film as current collector might be, and whether or not other metals or metal combinations could also serve as buffer layers (for instance Cu, or Al + Cu, both of which might also be more electrochemically stable than solely Al against lithium).

A different approach might be to modify the parameters of the IBDA deposition of Lipon to change the thermomechanical properties of the films. For example, it was reported that the thermal expansion coefficient of Lipon glasses decreases with increasing nitrogen content [8]. This also could conceivably reduce the thermal expansion mismatch sufficiently to alleviate the cracking problem.

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References

- [1] J.B. Bates, N.J. Dudney, G.R. Gruzalski, R.A. Zuhr, A. Choudhury, C.F. Luck, J.D. Robertson, 6th International Meeting on Lithium Batteries, *J. Power Sources* 43 (1993) 103.

- [2] X. Yu, J.B. Bates, G.E. Jellison Jr, F.X. Hart, J. Electrochem. Soc. 144 (1997) 524.
- [3] R.B. Goldner, P. Zerigian, T.Y. Liu, N. Clay, F. Vereda, T.E. Haas, Electrochem. Soc., Proc. 98-15 (1999) 268.
- [4] T. Aoki, Y. Nishikawa, S. Kato, Jpn. J. Appl. Phys. 28 (1989) 299.
- [5] M. Ohring, The Materials Science of Thin Films, Academic Press, NY, 1992.
- [6] R.C. Weast, M.J. Astle (Eds.), Handbook of Chemistry and Physics, 60th edn., CRC Press, 1980.
- [7] Properties of Corning's Glass and Glass Ceramic Families. Corning Publication PGGC-8/73-5M-HP, Corning Glass Works, Corning, NY 14830.
- [8] R.W. Larson, D.E. Day, J. Non-Cryst. Solids 88 (1986) 113.