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SPUTTER DEPOSITION OF LITHIUM SILICATE – LITHIUM PHOSPHATE AMORPHOUS ELECTROLYTES

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ABSTRACT

Thin films of an amorphous lithium-conducting electrolyte were deposited by rf magnetron sputtering of ceramic targets containing Li_4SiO_4 and Li_3PO_4. The lithium content of the films was found to depend more strongly on the nature and composition of the targets than on many other sputtering parameters. For targets containing Li_4SiO_4, most of the lithium was found to segregate away from the sputtered area of the target. Codeposition using two sputter sources achieves a high lithium content in a controlled and reproducible film growth.

INTRODUCTION

Lithium silicate – lithium phosphate glasses are promising materials for use as thin-film electrolytes in lithium cells. Amorphous films have been prepared using rf magnetron sputtering of ceramic targets containing Li_3PO_4 and Li_4SiO_4 in this and other laboratories [1-3]. Studies of the conductivity of these films have shown that a high lithium concentration is needed to minimize the film resistivity [4].

In this paper we demonstrate that the lithium content of the films is strongly dependent on the composition and homogeneity of the target used for sputtering. For targets containing Li_4SiO_4, there is a tendency for much of the lithium to segregate radially on the surface of the target, rather than sputter from the target. This segregation results in lithium deficient films when compared to the target composition. To our knowledge, such pronounced segregation has not been reported in the literature for this or any other ceramic material. Codeposition with multiple sputter sources is a reliable way to compensate for the lithium deficiency.

TARGET PREPARATION, SPUTTERING AND FILM ANALYSIS

Most films were prepared using a planar magnetron source designed to accommodate cylindrical targets approximately 1 inch in diameter by 1/8th inch thick. Targets were prepared from either the pure compounds, Li_4SiO_4, Li_3PO_4, and Li_2O, or from mixtures of these compounds. Most mixtures were prepared by grinding the components together; other mixtures were ground and calcined at 800°C several times in order to prereact the silicate and phosphate compounds. The powders were then either cold pressed into pellets and sintered in air at 900-1100°C or hot-pressed at 5000 psi and 1000°C. Li_2O targets were sintered at 700°C in dry nitrogen. Typical target densities relative to the theoretical density were 75% when sintered and 96% when hot pressed. As expected, the conductivity of targets composed of mixed lithium orthosilicate and lithium orthophosphate is much higher than that of the pure compounds [5,6]. The conductivity of the target is taken as a good indication of the degree of solid solution formed by the silicate and phosphate phases and increased in order from sintered mixtures to hot-pressed mixtures to sintered or hot-pressed targets made from the prereacted mixtures.

All targets were sputtered at 13.56 MHz at a constant forward power between 12 and 40 watts. Typically, the sputtering atmosphere was either pure argon or a 3:2 mixture of argon and oxygen at a total pressure of 20 mT. Ultra high purity gases were used with a total flow of 10-20 sccm. For a single source deposition, the film substrates were mounted parallel to and directly above the sputter target at 5-6 cm from the surface of the target. A quartz oscillator rotated into the substrate position was used to monitor the deposition rate before and after each film growth. Most film growths required times of 12-36 hours to achieve a film thickness

>1μm. Films were grown on electrically isolated substrates of glass, graphite, sapphire, and alumina. The temperature of the substrate holder increased during the film deposition reaching temperatures as high as 60°C. The species produced by the sputtering have been identified by emission spectroscopy of the plasma and by quadrapole mass spectrometry as described in Ref. 7.

The composition of the films were analyzed using a number of different techniques. These include energy dispersive x-ray analysis, photon induced gamma emission, atomic emission spectroscopy, and Rutherford backscattering spectroscopy. The details of each of these measurements and a complete discussion of the uncertainties will be given elsewhere. The agreement between the different analyses is reasonably good and the cation composition of the films is estimated to be accurate to ±10%. The films are assumed to be fully oxidized.

RESULTS AND DISCUSSION

In our planar magnetron sputtering source, the target material is mounted above two permanent magnets of opposite polarities. The center magnet is cylindrical and the outer is a concentric ring. The magnets act to concentrate the plasma in a ring near the surface of the target, so that the target is not sputtered uniformly, but rather develops a circular erosion groove [8]. Sputtering of the center and rim of the targets is generally negligible.

Targets of mixed Li_4SiO_4 and Li_3PO_4 have been made in a range of compositions. Most of the results presented here are for targets with approximately equal molar ratios of the two components, indicated as 1:1 Li_4SiO_4:Li_3PO_4. Similar results have been observed for a variety of targets with compositions that ranged from 1:8 to 3:2.

Figure 1 shows the appearance of three different 1:1 targets after sputtering in Ar + O_2 for an extended time (> 24 h). In each case, there is a mound of material at the center of the target and a protruding ring of material near the outside edge. The appearance, color, and thickness of this material at the rim and center of the target varies greatly, not only from target to target, but also around a single target. The color can range from pure white to very black for both sintered and hot-pressed targets when sputtered in Ar + O_2. The material at the center and rim of a target are always black when sputtered in pure argon. White crusts tend to be thicker than black ones. X-ray diffraction analysis of a number of samples taken from the material segregated at the center and rim of the targets is always identified as Li_2O. Presumably, the color is related to the stoichiometry of the oxide.

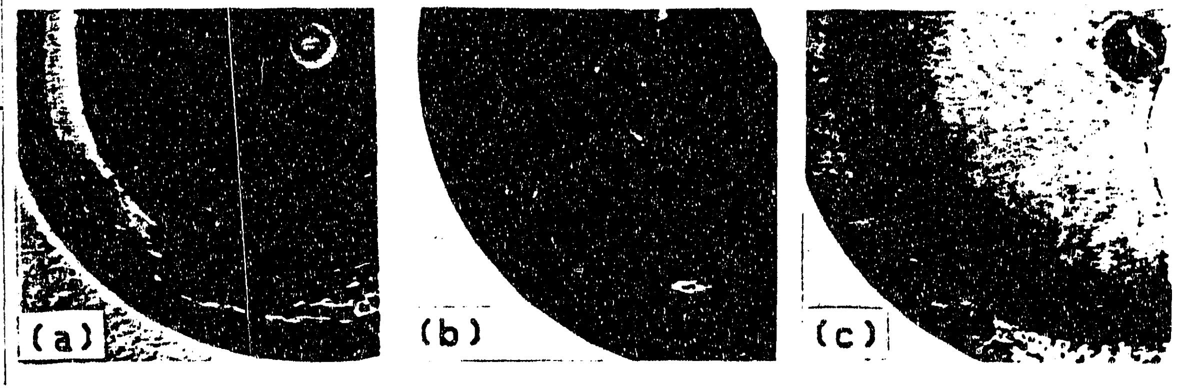

Fig. 1. Sections of Li_4SiO_4 + Li_3PO_4 targets after sputtering in Ar + O_2. Composition of each target is approximately 1:1. (a) sintered target from mixed powders, (b) hot-pressed target from mixed powders, and (c) sintered target from mixed and calcined powders.

The amount of Li_2O segregated to the center and rim of the targets is often very large, much more than would result from any resputtering of the growing film. This is illustrated by the cross section sketch shown in Fig. 2. There is clearly a large addition of material above the original surface of the unsputtered target. To our knowledge, such an effect has never been reported for the sputtering of ceramic materials. The relative amount of segregated material at the rim versus center of the target appears to vary with the rf power and the sputtering history of the target. At lower powers, most of the Li_2O segregates towards the center of the target rather than to the rim.

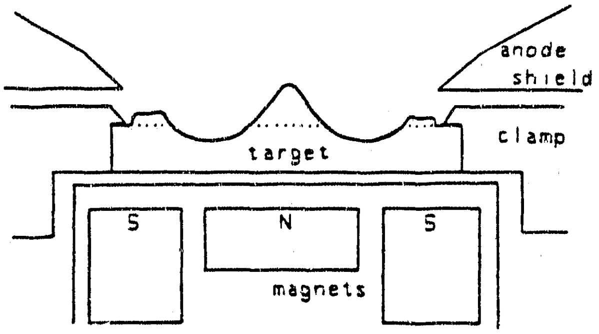

Fig. 2. Scale drawing of a cross-section of a typical 3:2 target after sputtering. The magnets and aluminum support plate of the sputtering source are also shown.

The first three entries of Table 1 show typical film compositions that have been grown from Li_4SiO_4:Li_3PO_4 (1:1) targets. Note that the relative Si and P contents in the table sum to 1.0 such that a film with a composition near that of the sputtering target would have a cation ratio of 3.5 Li : 0.5 Si : 0.5 P. It is not surprising that the lithium content is far below that of the original target compositions, as much of the lithium remains on the surface of the target. The relative silicon to phosphorous compositions, however, are very close to the compositions of the mixed targets. The differences observed for the sintered versus hot-pressed targets are interesting. Films grown from targets prepared by sintering the mixed powders are very lithium deficient and the magnitude of the ionic conductivity varies tremendously from film to film, over four orders of magnitude. Films grown from targets of hot-pressed powder mixtures generally have a much higher conductivity and higher lithium content. To determine if this difference can be attributed to either the higher target density or homogeneity achieved by hot-pressing, sintered and hot-pressed targets were made from a well calcined $Li_4SiO_4 + Li_3PO_4$ solid solution. The powder is likely still two-phase [6], but there is clearly a lot of mutual solubility. Surprisingly, films sputtered from hot-pressed pellets of the calcined powder had low lithium contents and conductivities comparable to films from the low density sintered targets (see Table I). Clearly factors other than the target density affect the sputtering yield of lithium from the target.

TABLE I. SPUTTERING CONDITIONS AND RESULTING FILM COMPOSITIONS

Target(s)	Sputter gas	Power (watts)	Depos. rate (Å/m)	Film composition Li : Si : P
1:1(mixed, sintered)[a]	Ar+O_2	20	8-9	0.35 : 0.53 : 0.47
1:1(mixed, hot-press)[a]	Ar+O_2	20	11-12	1.46 : 0.52 : 0.48
1:1(calcined, hot-press)[a]	Ar+O_2	20	6-11	0.33 : 0.54 : 0.46
$Li_4SiO_4 + Li_3PO_4$[b]	Ar+O_2	18/30	4-6	2.45 : 0.45 : 0.55
1:1 + Li_2O[b]	Ar+O_2	18/25	6-7	2.12 : 0.45 : 0.55
1:1 + Li_2O[b]	Ar only	15/30	8-11	3.04 : 0.51 : 0.49

[a] Single target prepared of mixed or calcined Li_4SiO_4:Li_3PO_4.
[b] Two targets used for codeposition.

Author's Name Dudney

page 3 of 12

Films were also grown by codeposition using two separate sputtering sources. Examples of codeposited films are listed as the last three entries in Table I. Most often the sources were pure sintered lithium orthosilicate and lithium orthophosphate targets. This technique has the advantage of allowing a wide range of film compositions to be grown from the same set of targets. Films have been grown with Si/P ratios ranging from 6/94 to 95/5 simply by adjusting the rf power applied to each source to give the desired relative deposition rates.

Figure 3 illustrates the geometry used for the dual source codepositions and the resulting film composition. For films 1 to 1.5 cm wide, the Si/P concentration varies approximately ±10% across the film. However, the conductivity measurements are always made at the center of the films where the Si and P composition varies only 2-3%. Homogeneity is improved by increasing the substrate-target distance, but the deposition rate is sacrificed. An alternative would be to rotate the substrate during film growth.

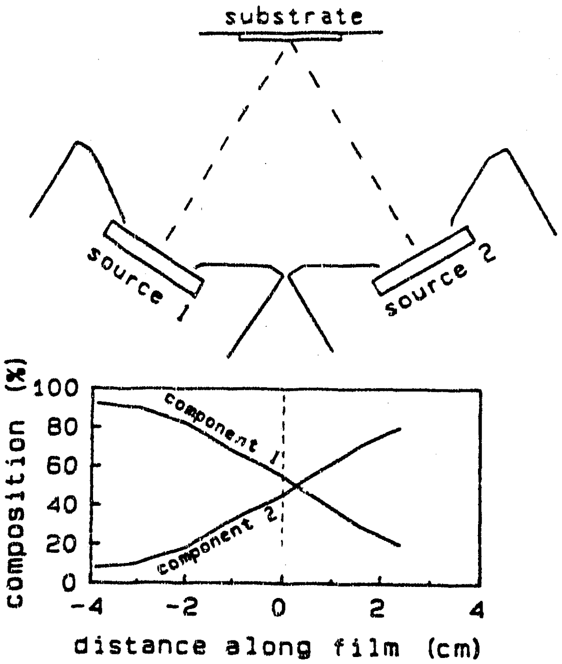

Fig. 3. Scale drawing through center of two sputter sources used for codeposition of films. Target to substrate distance is 5.9 cm. Plot shows observed film composition along plane of the figure. Dashed line indicates center point between the sources.

As shown in the table, the film prepared by the codeposition of Li_4SiO_4 and Li_3PO_4 contains more lithium than does the film from the hot-pressed 1:1 target of mixed powders. The conductivity is also improved by a factor of two. In general, films obtained from this dual source technique contain more lithium than those with a comparable Si:P concentration made by sputtering a single target. This observation must be due to the fact that pure Li_4SiO_4 and Li_3PO_4 sputter very differently.

Observation of the sputtered targets of the pure Li_4SiO_4 and Li_3PO_4 compounds made it obvious that the lithium segregation occurs almost exclusively on the silicate targets. No thick crusts of segregated Li_2O are formed on the Li_3PO_4 targets during sputtering, and consequently the films produced have nearly the same composition as that of the orthophosphate target. From the orthosilicate targets, however, the films contain at best only one fourth the lithium content of the target. The reason for such different behavior between the seemingly similar Li_3PO_4 and Li_4SiO_4 compounds is not understood. The materials have a similar crystal structure, melting temperature, and lithium conductivity [5,6]. However, there must be a significant difference in the free energy of formation [9], as we observe that Li_3PO_4 is less reactive with CO_2 than Li_4SiO_4. From mass spectrometry performed in our laboratory, no significant difference in the sputtered species have been observed for Li_4SiO_4 versus Li_3PO_4 targets. For both compounds, the sputtering produces simple atomic or small molecular species, such as Li_2O, Li, P, PO, Si, and SiO, for both the Ar + O_2 and Ar only sputter gases [7].

A number of experiments have been undertaken to try to characterize and perhaps minimize the lithium segregation that occurs on the Li_4SiO_4 targets. This work will be discussed in a separate publication. To date, changes in the sputtering conditions and changes in the lithium silicate targets have had little effect on the tendency for the lithium to accumulate away from the plasma area.

To further increase the lithium content of the films, it is necessary to compensate for the lithium loss at the silicate targets. Others have done this by adding excess lithium oxide powder or chunks to the mixed phosphate + silicate targets [2,3,10]; however, this is an unreliable way to control the film composition. We have used a Li_2O sputter source to compensate for the lithium loss of a 1:1 target. As shown in the table, films with much higher lithium contents, approaching (Li_4SiO_4 + Li_3PO_4) compositions, can be grown in this way. The table includes results for both the typical Ar + O_2 sputter gas mixture and also an Ar only deposition. Like the Li_4SiO_4 target, there is considerable redistribution of material on the Li_2O targets. In the Ar only atmosphere, this redistribution occurs more slowly, greatly increasing the life of a target. There is no evidence that the films are oxygen deficient when prepared in an argon only sputter gas.

Even when the sputter gas is pure Ar, the Li_2O deposition rate is more difficult to control than the lithium silicate or lithium phosphate sources. There are often large changes in the rate over time for a constant forward power. A more reliable way to control the Li_2O source is to monitor the Li emission in the plasma [7]. Figure 4 compares a spectrum recorded when a 1:1 target was sputtered alone (top) with one recorded during cosputtering of the 1:1 target with a Li_2O target (bottom). There is a large enhancement in the Li(670.8 nm) peak due to the extra lithium from the Li_2O source, while the relative intensities of the other peaks, mostly Ar

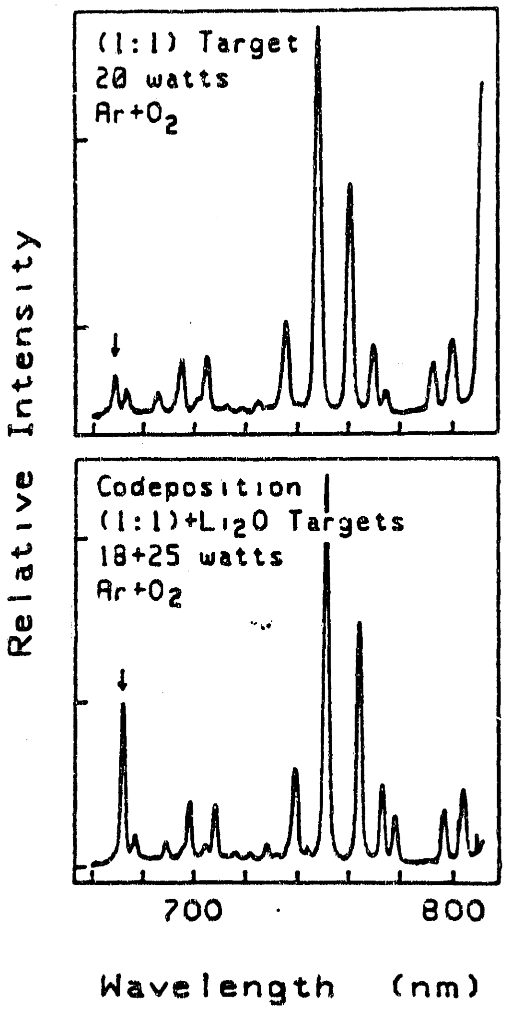

Fig. 4. Optical emission spectra for (a) single source with a 1:1 target, and (b) dual source with a 1:1 and a Li_2O target. Li emission line is indicated. Other peaks are due to Ar and O_2.

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emission lines, remain unchanged. The lithium emission could be used as a feedback to adjust the power for the Li_2O source in order to maintain a constant concentration during the film growth.

SUMMARY

Thin films have been deposited by rf magnetron sputtering from Li_4SiO_4, Li_3PO_4, and Li_2O ceramic targets. Single source depositions using targets of mixed $Li_4SiO_4 + Li_3PO_4$ phases lead to lithium deficient films, as much of the lithium in the target segregates on the surface away from the sputtered area. Pure Li_4SiO_4 targets also exhibit this lithium segregation, while pure Li_3PO_4 targets sputter nearly stoichiometrically. Codeposition using a Li_2O target can be used to compensate for the loss of lithium at the Li_4SiO_4 containing targets.

For more flexibility and control of the film composition, sputtering could be done from three independent sputter sources, such as Li_3PO_4, SiO_2, and Li_2O. The optical emission of the plasma could be used to continuously monitor and control the lithium concentration in the plasma. To improve the lateral homogeneity of the film, the substrate could be rotated during film deposition.

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