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Effect of Deposition Conditions On Microstructure of LiPON Films Obtained by RF Magnetron Sputtering

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***Abstract* — Thin conductive amorphous lithium phosphorous oxynitride (LiPON) films were prepared by rf magnetron sputtering in various experimental conditions. rf power, temperature of substrate, pressure of working gas and deposition time were varied. The microstructure of the films has been investigated by scanning electron microscopy and phosphorous mappings. The optimal conditions of reactive sputtering have been determined, which allows the formation of dense, homogeneous, free of cracks, amorphous thin LiPON films, and stable under ambient atmosphere. An ionic conductivity of $3.2 \cdot 10^{-6}$ S·cm^{-1} at room temperature has been determined by impedance spectroscopy.**

Keywords — ***LiPON films; RF magnetron sputtering; SEM; impedance spectroscopy.***

III. Introduction

The development of special portable electronic devices (smart cards, implantable medical devices, devices for fast data backup and so on) makes actual the development of energy-autonomous micro batteries. For independent power supply, solid-state thin film Li batteries are of great interest.

The inorganic amorphous thin films of lithium phosphorous oxynitride (referred to as LiPON) are promising material as electrolyte in solid-state thin film lithium batteries. Bates et al. were the first to report the preparation of amorphous LiPON films by rf magnetron reactive sputtering of lithium orthophosphate in nitrogen-containing atmosphere [1,2]. The LiPON films have an ionic conductivity around 10^{-6} S·cm^{-1} at room temperature with a very low electronic conductivity and a large electrochemical voltage stability (around 5 V at 25°C). Further, they are chemically inert in contact with metallic lithium. These properties allow the use of LiPON films for the development of solid-state thin-film Li batteries [3-6].

The electrical properties and microstructure of LiPON thin film are often affected by the different parameters used during the sputtering process. The main parameters are the rf power applied to the target, the pressure of working gas, the substrate temperature, the ratio of working gases, the distance between the target and the substrate. So, important requirements to the rf sputtering device is the possibility to vary the above-mentioned parameters in wide ranges. Unfortunately, such variation often is limited by technical reasons. For example, it was shown that the conductivity of LiPON film prepared by rf magnetron sputtering in pure N_2 is significantly increased with decreasing nitrogen pressure [7].

This is explained by the fact that decreasing the nitrogen pressure during deposition of LiPON film leads to an increase of the concentration of 3-coordinated nitrogen atoms -N< (Nt) as compared to 2-coordinated nitrogen atoms -N= (Nd). The conductivity increases with increasing (Nt)/(Nd) ratio. The information about the effect of sputtering power on the conductivity of LiPON films is controversial. When sputtering power is decreased, either an increase [8,9] or a decrease [10] in conductivity can be reported. The conductivity of LiPON film increases with increasing of temperature of substrate during the sputtering [11]. The LiPON films conductivity depending on the nitrogen flow rate has a maximum. The maximum value of $3 \cdot 10^{-6}$ S/cm^{-1} is observed at nitrogen flow rate of 40 mL/min [12,13]. However, the effect of rf magnetron sputtering conditions on the microstructure of LiPON film is very seldom described.

The deposition rate of the film can be increased by using other deposition techniques, including plasma assisted deposition [14,15] or ion beam assisted deposition [16]. However, to date the highest value of conductivity is observed in the LiPON films obtained by rf magnetron sputtering. That is why in this paper, the classical method of rf magnetron reactive sputtering, with the possibility to vary in a wide range the main parameters of the reactive sputtering, was used.

The aim of this study was to investigate the effect of deposition conditions by magnetron sputtering (rf power, substrate temperature, deposition time, and the pressure of nitrogen as working gas) on the microstructure and electrical properties of LiPON film.

IV. Experimental Details

LiPON films are deposited by rf magnetron reactive sputtering using pure nitrogen (99.96 %) as a working gas, and lithium orthophosphate, γ-Li_3PO_4, as a target.

For the synthesis of lithium orthophosphate, phosphoric acid is neutralized by saturated solution of extra-pure lithium hydroxide. The precipitate is dried at 150°C for 5 hr and calcined at 550°C for 2 hr. The obtained powder is milled in ethanol for 6 hr using agate grinding balls. The mixed slurry is dried, sieved, mixed with a solution of polyvinyl alcohol (5 w %) as a plasticizer and finally pressed. The pressed pellets are further sintered at 850°C for 3 hr. The sintered pellets have a density of 2.2 g/cm^3 and are used to prepare the target of 40 mm of diameter and 3 mm of thickness.

To investigate the influence of different sputtering parameters, such as rf power, substrate temperature, sputtering time, working gas pressure, on the properties of LiPON films, the rf magnetron sputtering setup was improved. LiPON films were deposited on different types of substrates including polycrystalline α-Al_2O_3, amorphous glass, Si wafer with n-type conductivity (n-Si). The substrates were cleaned with solutions of acids and organic solvents in an ultrasonic bath before deposition.

Phase composition of the target and deposited films were examined by X-ray powder diffractometry (DRON-4-07, Bourevestnik and D8 Advance, Bruker) using CuKα radiation. The film thickness was measured using a Dektak profilometer (Veeco). The microstructure of the films was studied by optical and scanning electron microscopy (SEM) operating at 20 kV. The films were covered with a thin C film. The films were also characterized by Energy-Dispersive X-ray analysis (EDX) coupled to the SEM microscope.

FTIR spectroscopy was carried out on a Bruker IFS 66 spectrometer in transmission mode using a DTGS detector. The spectra were recorded in the spectral range of 400-4000 cm^{-1} with a resolution of 2 cm^{-1}.

The electrical conductivity measurement was carried out on LiPON film in a planar configuration at room temperature under dry N_2. LiPON film, 3.5 µm thickness, has been deposited onto glass substrate (11 x 25 mm) onto which two Al electrodes, separated by 15 mm gap, have been previously sputtered. This cell has a high form factor of 3900 cm^{-1} but in this way any short circuits are avoided. A Frequency Response Analyzer (Solarton 1260) and a Dielectric Interface (Solartron 1296) were used in the frequency rage from 1Hz to 1 MHz.

V. Results and Discussion

A single-phase high-temperature orthorhombic γ-Li_3PO_4 (space group Pmnb: a = 0.6114 nm, b = 1.047 nm, c = 0.4922 nm [17]) is observed. The diffraction pattern of LiPON film deposited on n-Si substrate without substrate heating. The pattern does not reveal any diffraction peaks of crystalline phases but only a broad peak in the range 2θ = 15-35º, indicating amorphous nature of the film, as previously reported by different authors [5,10,18-21]. Such pattern has been obtained for all the films prepared without substrate heating, regardless of the rf power, the pressure of nitrogen working gas and the deposition time.

Fig. 1 (curves 1-4) shows the XRD patterns of LiPON deposited on α-Al_2O_3 substrate without substrate heating (curve 2), with a substrate temperature of 200°C (curve 3) and with a substrate temperature of 400°C (curve 4). The XRD spectrum of α-Al_2O_3 substrate alone is shown in curve 1. The diffraction peaks observed in curve 2 can be assigned to the substrate indicating once more that LIPON film is amorphous when deposited without substrate heating. When the substrate temperature increases, new diffraction peaks emerge from the broad peak (curve 4) indicating the deposition of a crystalline phase which can be related to the Li_3PO_4 or LiPON.

Unfortunately, the diffraction peaks of Li_3PO_4 and LiPON are very similar and it is impossible to distinguish these phases from XRD data and to evidence the incorporation of nitrogen atoms in the film by this diffraction technique.

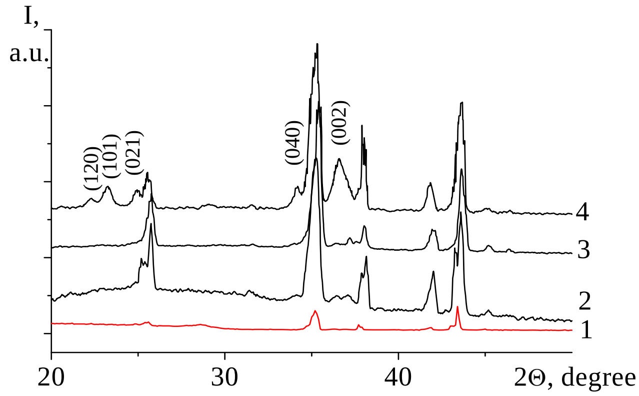

Fig. 1. XRD patterns of α-Al_2O_3 substrate (1) and LiPON film on α-Al_2O_3 substrate: without heating (2), 200°C (3), 400°C (4).

Fig. 2 shows the infrared IR spectra of the LiPON films deposited on n-Si substrate measured from 2000 to 450 cm^{-1}. The IR spectrum of single crystal substrate n-Si contains a small amount of weakly intense peaks. IR spectrum of Li_3PO_4 film on n-Si substrate contains peaks of the substrate and addition peaks coming from the deposited film. They can be ascribed to Li-O-P groups at 450-585 cm^{-1}, 850-925 cm^{-1} and 1450-1500 cm^{-1} [22], P=O groups at 1000-940 cm^{-1}, and P–O groups at 915–880 cm^{-1} [21-23]. IR spectrum of LiPON film on n-Si substrate contains peaks of the substrate and addition peaks. In comparison with the IR spectrum of Li_3PO_4 film, the peak intensities of phosphate groups and Li-O-P groups (850-925 cm^{-1}) are changed. On the IR spectrum of LiPON film in the range 1300-1250 cm^{-1} and 1680-1600 cm^{-1}, new peaks are observed. These peaks can be ascribed to the following groups [24]: -P-N=P (1680-1600 cm^{-1}), -P-NP_2 (1300-1250 cm^{-1}).

In the remaining part of this paper, the influence of the sputtering parameters, i.e. the substrate temperature, the rf power, the sputtering time and the pressure of N_2 working gas, on the microstructure of LiPON film was shown. The experimental conditions used are summarized in Table 1.

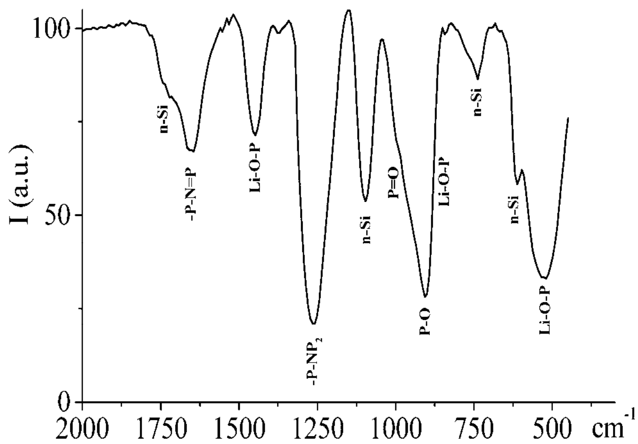

Fig. 2. IR spectra of the LiPON film on n-Si substrate.

3.1. Effect of the substrate temperature.

LiPON films have been deposited onto α-Al_2O_3 substrates with a 2.2 W/cm^2 rf power for 2 hr under a N_2 pressure of 100 mTorr. The properties of films deposited at different temperatures of the substrate have been studied, i.e. no heating of the substrate, 200°C and 400°C. Fig. 3 (a, b and c) shows the SEM micrographs of LiPON films. Fig. 3 (a', b' and c') shows the phosphorous mapping corresponding to the SEM images (for P mapping: yellow, orange or red colors correspond to the presence of P in the film, whereas black color corresponds to the absence of P in the film). Finally Fig. 3 (a'', b'' and c'') presents the EDX analysis of the sample surface showing O (from α-Al_2O_3 substrate and LiPON film), Al (from substrate) and P (from film). Carbon comes from the deposition of the thin layer of C on the LiPON film to avoid electrical charging of the sample and to obtain good quality of images. Nitrogen can not be detected by EDX analysis because of the too small amount contained in the films. The film deposited without external substrate heating (Fig. 3 a') has an island structure (red areas) with some amount of non-deposited areas where film is absent (black). An island structure of the film is formed due to low deposition time (2 hr). The film deposited on the substrate heated at 200°C (Figs 3 b, b', b'') has P present on the entire film (orange) with small spots of high concentration of P (yellow) where the presence of Al is not visible. The EDX spectrum shows that the film deposited without external substrate heating contains the higher amount of phosphorus (high ratio P/Al) comparing to the films prepared with external substrate heating (Figs 3 a'', b'', c''). This fact indicates the higher thickness of this LiPON film. The difference observed in the microstructure of the films deposited at different temperatures can be explained by the theory of film formation [25].

Following this theory, particles are sputtered from the target by the ions of the plasma (mainly N^{3+} ions) and collide with the substrate. After the collision, the particles can act by 3 ways. First, the particles can be adsorbed and afterwards can condense to the substrate. Second, after being adsorbed the particles can be desorbed and then leave the substrate. Third, the particles can be immediately reflected from the substrate.

TABLE I. PARAMETERS OF SPUTTERING OF LIPON FILMS

Parameters	Deposition mode
Composition	Li_3PO_4
size of target	40 mm diameter, 3 mm height
pressure in chamber	$5 \cdot 10^{-4}$ mTorr
Working gas	Nitrogen (purity 99.96%)
Distance target/substrate	4 cm
Substrate	α-Al_2O_3, Glass, n-Si
N_2 pressure in chamber	10 mTorr, 100 mTorr
rf power (W/cm^2)	0.7, 2.2, 4.4
Substrate temperature	25ºC, 200ºC, 400ºC
Deposition time	2 hr, 5 hr, 10 hr

Only by the first way dense uniform film can be formed. In this case the adsorbed particles may migrate along the substrate surface, collide with other particles and form cluster-nucleus. These clusters may growth using adsorbed particles and the surrounding region (referred to as lock-in zone) becomes depleted. In the lock-in zone, new particles adsorb, migrate towards the nucleus, and increase their size. With the growth of nucleus, lock-in zone is narrowed. Finally, nucleus associate and form a dense uniform film. Hence according to this process the film initially should always have an island structure, which is observed in Fig. 3a. The interactions of the particles with the substrate, as well as the ways of the film formation, are determined by the parameters of deposition. The interaction between substrate and particles mainly depends on the temperature. The way of the film is formed may depend on the action of several parameters. Namely, when the substrate temperature increases up to 200ºC, desorption of particles is favored and then island film structure is saved (fig. 3b), so more time is needed to achieve uniformity. In this case both the substrate temperature and the deposition time are important parameters to obtain a continuous film. When substrate temperature increases to 400°C, no new clusters are formed (Fig. 3 c, c'). In this case, the size of islands increases, but the phosphorus content in the film decreases (Fig. 3 c''). This contradiction can be explained by the fact that the islands grow only at the surface of the film, so halos around the islands are visible (Fig. 3 c). A similar fact is described in [26] where it is shown that under certain conditions, the structural and chemical transformations (including decomposition of amorphous phase on the lithium- and phosphorus-containing components) occurs in LiPON films.

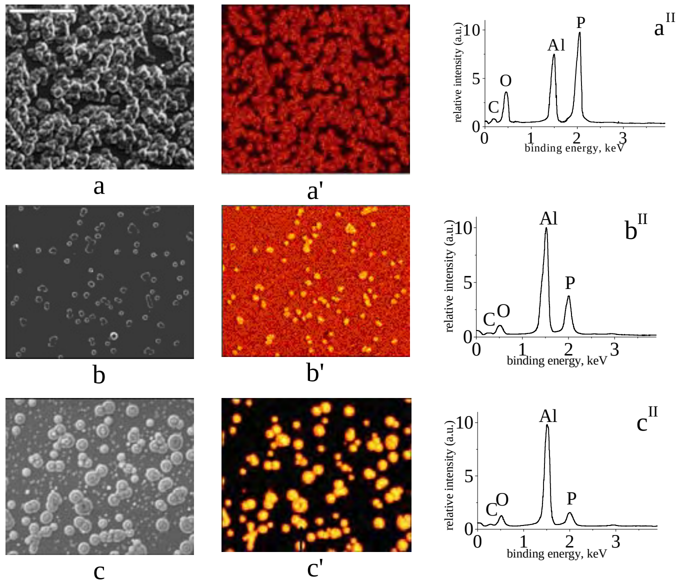

Fig. 3. Microstructure of LiPON films deposited on α-Al2O3 substrates without heating (a), at 200°C (b) and at 400°C (c). Phosphorus distribution in LiPON films on α-Al2O3 substrates deposited without heating (a'), at 200°C (b') and at 400°C (c'). EDX spectra of LiPON films on α-Al2O3 substrates deposited without heating (a''), at 200°C (b'') and at 400°C (c'').

The products of decomposition are not uniformly distributed on the surface and in the volume of the film. Nimisha et al. assumed that these products locally crystallized in the centers of the islands [26]. However, these processes are not dependent on the deposition mode. We found that at 400°C, crystalline phase is formed in LiPON film (see Fig. 1, curve 4) and low phosphorus content can be explained by the decomposition of $Li_{3+y}PO_{4-x}N_{(y+2x)/3}$ phase.

Our research shows that at high substrate temperature, structural and chemical transformations occur in $Li_{3+y}PO_{4-x}N_{(y+2x)/3}$, which leads to a non-uniform distribution of matter in the volume and at the surface of the film. At low deposition time (2 hr), these processes are accompanied with the formation of films with island structure containing crystalline phase. Therefore the films deposited without external substrate heating were investigated in the remaining part of this paper.

3.2. Effect of the rf deposition power.

Films have been sputtered on glass substrates without substrate heating in pure nitrogen during 10 hr at different rf powers, i.e. 10, 30 and 60 W corresponding to 0.7, 2.2 and 4.4 W/cm^2 respectively. At low rf power (0.7 W/cm^2) the film thickness was less than 1 μm and the films had an island structure with micron-sized spherical particles. At high rf power (4.4 W/cm^2) the film thickness was greater than 3 μm, characteristic of a high rate of deposition. These latter films had a rough structure and were not stable over time. When films were stored in air, cracks appeared on their surface.

It should be noted that according to the literature, the rf deposition power influences also the content of bounded nitrogen in the $Li_{3+y}PO_{4-x}N_{(y+2x)/3}$ film. The higher the rf power, the lower the ratio N/P in the films (ratio obtained by XPS). Therefore at high rf power and then relative high rate of deposition, N atoms not only substitutes O to form $Li_{3+y}PO_{4-x}N_{(y+2x)/3}$ solid solution but can also be captured as N_2 gas molecules in the film and released after some time of storage leading to cracks. At intermediate rf power (2.2 W/cm^2), homogeneous, continuous and stable films were formed. It is clearly shown in this study that rf power influences greatly the microstructure of the deposited films. A homogeneous, continuous and stable film can be prepared with our equipment at 2.2 W/cm^2.

3.3. Effects of the sputtering time and N2 pressure.

Although in the literature we can observe that there is a tendency to avoid long time of sputtering, there is no systematic study of the influence of the sputtering time on the microstructure of LiPON films.

Films have been deposited on glass substrates, at 2.2 W/cm^2 rf power, without heating substrate and at a N_2 pressure of 100-mTorr. Deposition times were 10 hr or 5 hr. The film thickness increases with time, and the deposition rate was constant, ca 5 nm/min in these experimental conditions.

The film obtained after 5 hr of sputtering was 1.5 μm thick and the film obtained after 10 hr of sputtering was 3.1 μm thick. After 10 hr of sputtering and at N_2 pressure of 10 mTorr, a continuous film is formed, in which cracks are observed (Fig. 4 a, b). When the deposition time decreases until 5 hr, the size of cracks in LiPON film decreases.

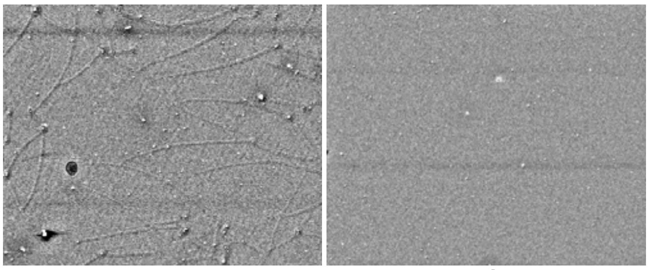

Fig. 4. LiPON film deposited on a glass substrate without heating, at 2.2 W/cm2 rf power, for 10 hr (a) and 5 hr (b) under 10 mTorr of pure N2 (x400).

EDX P mapping shows that both films have homogeneous and continuous P distribution. It should be noted that Vereda et al. [27] observed the formation of cracks in LiPON films, if they had undergone a temperature change from 300°C to room temperature. This fact was explained by a mismatch between the coefficients of thermal expansion of LiPON film, glass substrate and metallic electrode introducing mechanical stress in the film and cracks during heating/cooling.

Our results show that the cracks in LiPON can be formed during the film deposition. It can also be postulated that high N_2 pressure favors the introduction of N_2 molecules during sputtering that can be released during or after deposition and formed cracks in the film. Therefore, in the remaining part of this paper, the films deposited at a lower N_2 pressure, ca 10 mTorr, have been investigated.

3.4. The conductivity of LiPON films.

The conductivity of these films, prepared under the optimal conditions has been determined by impedance spectroscopy. Fig. 5 show the impedance diagram of LiPON film in Nyquist plane obtained under dry N_2 at room temperature. The conductivity at 20°C of $3.2\cdot10^{-6}$ S·cm^{-1} has been determined. Using data of impedance spectroscopy, the temperature dependence of LiPON film has been plotted (Fig. 6), and the activation energy of conductivity has been calculated (0.27 eV).

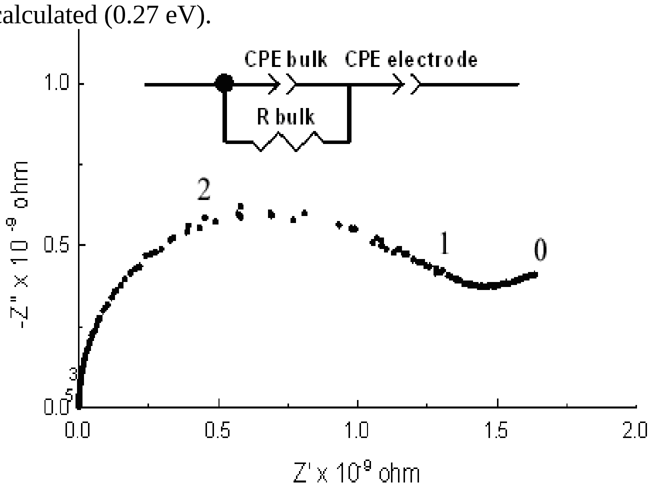

Fig. 5. Complex impedance diagram in the Nyquist plane of LiPON film recorded under dry N2 at room temperature. The numbers near the curve indicate the log of the frequency.

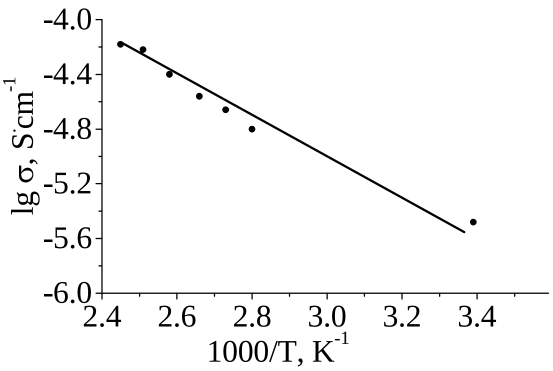

Fig. 6. Temperature dependence of the conductivity of LiPON film.

This is in good agreement with the value generally reported in the literature [1,2,4,19,18,28]. Further, impedance spectra have been recorded under dry air every hour for 16 hours. These spectra overlap perfectly indicating that these films are stable under dry air.

VI. Conclusions

The microstructure of the lithium-ion conductive amorphous LiPON films, deposited by rf magnetron reactive sputtering has been investigated. The influence of the parameters used during sputtering, i.e. the rf power applied to the target, the substrate temperature, the deposition time and the pressure of working gas, on the microstructure of the films has been studied. It has been shown that the heating of the substrate during sputtering as well as the incorporation of N_2 molecules in the film, deposited at high pressure of N_2, has a dramatic impact on the microstructure of the films. The optimal parameters of LiPON films deposition have been determined (the rf power density 2.2 W/cm^2, no heating of the substrate, a deposition time of ca. 5 hr and a nitrogen pressure of 10 mTorr), in order to obtain an homogeneous, cracks- and islands-free amorphous thin film. It has been shown that LiPON films deposited are stable under dry air and have the conductivity at 20°C of $3.2 \cdot 10^{-6}$ S/cm.

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