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Plasma properties during magnetron sputtering of lithium phosphorous oxynitride thin films

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HIGHLIGHTS

- LiPON thin films were investigated by FIB-SEM.
- Plasma parameters were measured by mass spectrometry, probes and emission spectroscopy.
- Best film conductivity is correlated with a higher degree of dissociation for N_2.
- Higher ion energy and larger fractions of Li, P and NP are also important.

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ABSTRACT

The nitrogen dissociation and plasma parameters during radio frequency sputtering of lithium phosphorus oxynitride thin films in nitrogen gas are investigated by mass appearance spectrometry, electrostatic probes and optical emission spectroscopy, and the results are correlated with electrochemical properties and microstructure of the films. Low pressure and moderate power are associated with lower plasma density, higher electron temperature, higher plasma potential and larger diffusion length for sputtered particles. This combination of parameters favors the presence of more atomic nitrogen, a fact that correlates with a higher ionic conductivity. Despite of lower plasma density the film grows faster at lower pressure where the higher plasma potential, translated into higher energy for impinging ions on the substrate, resulted in a compact and smooth film structure. Higher pressures showed much less nitrogen dissociation and lower ion energy with thinner films, less ionic conductivity and poor film structure with large roughness.

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1. Introduction

The increasing demand on portable microelectronic devices (sensors, circuit boards, etc.) has made the development of compact, all-solid-state thin film batteries a field of increasing importance. A common requirement for the batteries is that they need to be compact, of low weight and of high power density. Thus, improving the performance, i.e. capacity, lifetime and safety, and lowering the cost of batteries is a critical goal under stringent need for development. Lithium ion based batteries are often chosen due to their high power density and low weight. The main active components in a battery are the cathode, anode and electrolyte. The requirements for a good solid electrolyte includes a high ionic conductivity, low electronic conductivity, electrochemical stability in a wide potential range, good performance in a wide temperature range, homogeneous morphology without pores or cracks, and good adhesion with the electrode materials. Lithium phosphorous oxynitride (Lipon) [1,2] thin films is one of the most promising electrolyte materials for compact solid-state-battery [3–6]. It was initially developed in the 1990's by Oak Ridge National Laboratories and is an amorphous Li^+ ion conductor with a very high electrochemical stability window of between 0 V and 5.5 V vs. Li/Li^+ [7], which makes it compatible with high-voltage cathodes, as well as stable in contact with lithium metal [1]. In addition it shows an acceptable Li ion conductivity ($\sigma_{Li+} \approx 2 \cdot 10^{-6}$ S cm^{-1}) [7] and low electron conductivity ($\sigma_{e-} = 8 \cdot 10^{-14}$ S cm^{-1}) [8] at 25 °C depending on the exact stoichiometry, usually close to $Li_{3.3}PO_{3.9}N_{0.17}$ [1]. Due to the amorphous structure Lipon has the advantages of isotropic conduction properties and in addition it can form flexible thin films [9] and exerts no cracking even when cathode volume changes [7]. This makes it very interesting for commercial applications. Besides being used as solid electrolyte, Lipon is also interesting as a particle coating to stabilize high voltage cathodes [10–13].

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Several deposition techniques have been used to produce Lipon thin films, including: radio frequency (RF) magnetron sputtering [4,14–19], pulsed laser deposition [20], electron beam evaporation [21], ammonolysis [22], plasma assisted vapor deposition [23], and ion beam directed assembly [24]. Reactive magnetron sputtering is the technique most often used, where the Lipon thin films can be formed by sputtering from a Li_3PO_4 target in pure nitrogen gas. Many parameters of the sputtering process affect the quality of the Lipon films in terms of Li ion conductivity, film morphology, and film deposition rate. This includes RF sputtering power [14–16,19,25], nitrogen pressure [16,17,19], nitrogen flow rate [25,26], substrate temperature [27], post–thermal treatment [28,29], target morphology [18,19,25], and target-to-substrate distance [19]. During the sputtering the nitrogen atoms are incorporated into the Li_3PO_4 structure by breaking the P–O–P bond and forming P–N=P and P–N$<^{P}_{P}$ bonds [30]. The introduction of triple bonded nitrogen induces a structural disorder which affects the ionic conductivity of the film considerably, however, despite extensive research this dependence is not yet well understood [31]. A new approach to better understand how the sputtering parameters affects the Lipon properties is to determine the type of reactive species formed in the plasma during the reactive sputtering. Identification of the type and concentration of reactive species in correlation with main plasma parameters (plasma density, n_e, electron temperature, T_e, and plasma potential, V_{pl}) during the Lipon sputtering could thus contribute to the understanding of the film growth mechanism and then link it to the electrochemical properties. To our knowledge such kind of plasma diagnostics during sputtering of Lipon has never been reported.

The objective of this work is to investigate the plasma properties during the reactive RF magnetron sputtering of a Li_3PO_4 target in nitrogen atmosphere using mass spectrometry, electrostatic probes and optical emission spectroscopy. The detailed plasma diagnostic is performed in an electron cyclotron resonance (ECR) plasma assisted RF sputtering setup. The influence of sputtering power and nitrogen pressure on the reactive species formed in the plasma is investigated in direct correlation with morphology and electrochemical properties of deposited Lipon films. A sputtering power in the range of 50–300 W and a nitrogen pressure in the range of 5–50 mTorr will be used. Focused ion beam scanning electron microscopy (FIB-SEM) is used for characterization of the microstructure and film morphology and electrochemical impedance spectroscopy (EIS) is used for determining the ionic conductivity of the films.

2. Experimental methods

2.1. RF magnetron sputtering

The synthesis of thin Lipon films was performed using an RF magnetron sputtering system of a 2 inch Li_3PO_4 target (Kurt Lesker®) in N_2 atmosphere. The Li_3PO_4 target was presputtered for an hour before each deposition in order to remove any impurities of hydrocarbons on the surface. The Lipon films were deposited onto 100 nm Au-coated silicon substrates using different values of N_2 pressure (5, 20, or 50 mTorr) and RF power (100, 200, or 300 W) in a controllable nitrogen flow of 66 sccm. A sputtering time of 7 h and a target-to-substrate distance of 60 mm were used in each case. The substrate temperature (below 200 °C) was dictated by heat formation from the plasma generation and no additional heating was applied. A 300 nm Ag coating was deposited on top of the Lipon layer. Proper masking during deposition of the Lipon and Ag layers, resulted in Au/Lipon/Ag cells of 7×7 mm^2.

2.2. Impedance spectroscopy

The resistances of the Lipon films were measured by AC electrochemical impedance spectroscopy (EIS). The EIS spectra of the prepared single layer Lipon films was measured by using the Ag/Lipon/Au sandwich structure. A setup consisting of spring loaded Au-plated pins implanted in a Plexiglas plate was used for the EIS measurements in a 2-electrode setup. One of the test probes was contacted to the Ag film (using a piece of conducting rubber in between) and the other was contacted to the Au coated substrate outside the cell. EIS measurements were conducted at room temperature using a Biologic VMP3 impedance analyzer in the frequency range from 10 mHz to 500 kHz. Two cells for each Lipon layer type were tested. The impedance data were analyzed by nonlinear least square fitting of the data to equivalent circuits using the EC lab software [32].

2.3. Thin film characterization

The microstructure of Lipon films prepared at 100 W was investigated using a Carl Zeiss 1540 XB (Carl Zeiss, Oberkochen, Germany) combined focused ion beam and scanning electron microscope (FIB-SEM). A Ga-ion source was used for the FIB. To create a cross-sectional view perpendicular to the Ag surface, a trench was created using a 10 nA ion-probe and the subsequent surface polish was performed using a 200 pA beam. For the SEM, an acceleration voltage of 1.5–5 keV was used and either a secondary electron (SE) or an in-lens SE detector was used for obtaining the micrographs. Lipon films prepared at 200 W and 300 W were investigated using a Carl Zeiss Supra 35 (Carl Zeiss, Oberkochen, Germany) with an acceleration voltage of 1.5–5 keV. Cross sections were prepared by fracturing these samples inside the glove box with aid from a diamond cutter on the back side. The samples were very shortly exposed to air (less than 1 min) during the transfer between glove box and SEM. The XPS measurements were performed on a commercial PHI 5500 spectrometer (Perkin Elmer Physical Electronics, Minneap-olis, MN), using monochromatized Al Kα radiation (1487 eV) and an electron emission angle of 45°. The dimensions of the measurement region were approximately 2×4 mm.

Energy dispersive spectroscopy (EDS) measurements were performed using the Carl Zeiss Supra 35 at an acceleration voltage of 10 kV. Data was collected using a “Bruker Nano XFlash Detector” and analyzed by the software “Bruker Esprit 1.9”.

2.4. Plasma diagnostics

Surface contamination of probes, additional electrodes and optical ports is the main problem for plasma diagnostics during deposition of thin films by magnetron sputtering. Even a few seconds of deposition are enough to contaminate the probe surface; a fact that results in erroneous measurements of the current-bias characteristic and consequently incorrect estimation of plasma parameters [33,34]. Films above only a few nm deposited on windows keeping the vacuum or on tips of optical fibers can also affect the emission lines detected by optical emission spectroscopy. In addition, such films can also influence the performance of a separation mesh placed in the front of the orifice of the mass spectrometer to eliminate the contribution of plasma ions when detecting the neutral radicals. For these reasons a different setup than the one used to deposit micrometer thick Lipon films was used for plasma diagnostics. The following precautions were taken to ensure a correct diagnostics. An independent plasma source was used in the same chamber with the magnetron sputtering cathode and the diagnostic equipment as to allow the cleaning of the probe surface and of the separation mesh by ionic bombardment in nitrogen plasma during

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