

# Magnetron sputtering of lithium phosphorous oxynitride thin films

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Plasma parameters during RF sputtering of lithium phosphorus oxynitride thin films in nitrogen gas are investigated by mass appearance spectrometry and electrostatic probes, 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 favours 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.

## 1. Introduction

Lithium phosphorous oxynitride (Lipon) is one of the most promising electrolyte materials for compact all-solid-state-batteries [1]. Due to the amorphous structure Lipon has the advantages of isotropic conduction properties. It can be deposited by reactive magnetron sputtering when nitrogen atoms are incorporated into the  $\text{Li}_3\text{PO}_4$  structure by breaking the P-O-P bond and form P-N=P and P-N<P bonds. The introduction of triple bonded nitrogen induces a structural disorder which affects the ionic conductivity. Despite of extensive research this dependence is not yet well understood [2].

The objective of this work is to investigate the reactive RF magnetron sputtering of  $\text{Li}_3\text{PO}_4$ .

## 2. Experimental details and results

The Lipon thin films were deposited using a RF magnetron sputtering system of a 2 inch  $\text{Li}_3\text{PO}_4$  target (Kurt Lesker ®) onto 100 nm Au-coated silicon substrates using different values of  $\text{N}_2$  pressure (5, 20, or 50 mTorr) and RF power (100, 200, or 300 W) in a controllable 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 plasma. 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  $7 \times 7 \text{ mm}^2$ . The resistances of films were measured by AC electrochemical impedance spectroscopy (EIS) using the Ag/Lipon/Au structure. The impedance data were analyzed by nonlinear least square fitting of the data to equivalent circuits using the EC lab software. The microstructure of Lipon films was investigated using a Carl Zeiss 1540 XB (Carl Zeiss,

Oberkochen, Germany) combined focused ion beam and scanning electron microscope (FIB-SEM). The XPS measurements were performed on a commercial PHI 5500 spectrometer (Perkin Elmer Physical Electronics, Minneapolis, MN), using monochromatized Al K $\alpha$  radiation (1487 eV) and an electron emission angle of 45°. The dimensions of the measurement region were approximately  $2 \times 4 \text{ mm}$ . Energy dispersive spectroscopy (EDS) measurements were performed using the Carl Zeiss Supra 35. Data was collected by a “Bruker Nano XFlash Detector”.

Surface contamination of probes 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 [3]. For these reasons a different setup than the one used to deposit micrometer thick Lipon films was used for plasma diagnostics [4]. The 2 inch magnetron sputtering cathode was placed on the lateral side facing the head of a Hiden mass spectrometer, with a distance of 130 mm from the entrance orifice to the cathode. The Langmuir probe was inserted perpendicular to the direction of the mass spectrometer and the cathode (6.5 cm from the cathode surface in the axial direction and 2.5 cm off axis) as to measure plasma parameters. The current-voltage probe characteristics were used to obtain plasma density,  $n_i$ , from the ionic saturation region, the effective electron temperature,  $T_{\text{eff}}$ , by integrating the electron energy distribution function, and plasma potential,  $V_{\text{pl}}$ , as the potential giving the maximum value of the first derivative of the current-voltage characteristic.

Probe measurements of  $n_i$  as a function of RF power at different pressures revealed that the plasma density increased with RF power and also with nitrogen pressure in a range from  $5 \times 10^{15} \text{ m}^{-3}$  up to  $3 \times 10^{16} \text{ m}^{-3}$ . Fig. 1 shows  $T_{\text{eff}}$  and  $V_{\text{pl}}$  as a function of RF power for different pressures. The effective electron temperature was below 1.5 eV except for  $p=5$  mTorr and  $P_{\text{RF}} > 150$  W, and reached more than 2 eV only at 300 W and 5 mTorr. The plasma potential was 9 V at 5 mTorr and decreased to 4 V for  $p=50$  mTorr. One important observation is that due to acceleration in the potential difference between  $V_{\text{pl}}$  and the grounded substrate  $\text{N}^+$  can gain more than 9.5 eV at 5 mTorr and 100 W when reaching the substrate. This energy is very close to the dissociation energy of  $\text{N}_2$  of 9.79 eV which means that  $\text{N}^+$  can induce surface dissociation of  $\text{N}_2$  unblocking the N penetration, and even more creating additional reactive N.

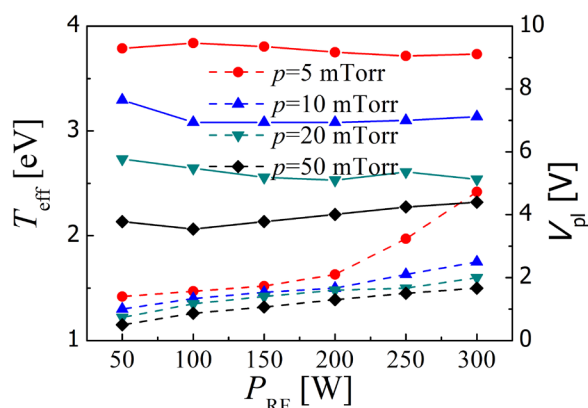


Fig. 1  $T_{\text{eff}}$  with dashed lines and  $V_{\text{pl}}$  with continuous lines as a function of RF power for different pressures.

Plasma parameters by mass spectrometry have shown a higher degree of nitrogen dissociation at low pressure (below 10 mTorr) and moderate discharge power (below 150 W). More atomic N and also Li, correlated with higher ion energies, and formation of NP bonds in the gas phase, were very well correlated with thin films with higher ionic conductivity, higher deposition rate and smoother and more compact films.

To correlate the amount of atomic nitrogen in gas phase with film properties the film composition was investigated by XPS and EDS. Fig. 2 presents the (a) N1s and (b) P2p peaks by XPS for 5 and 50 mTorr, respectively, deposited

for 100 W and 150 min deposition time (about 300 nm in film thickness deposited on 0.5 mm thick silicon substrate). Despite of higher  $\text{N}_2$  pressure the N1s peak was higher at 5 mTorr than at 50 mTorr. A reversed trend was observed for P2p with larger content of P for 50 mTorr. The deconvolution of experimental peaks has revealed comparable fractions of double and triple coordinated N bond structure for 5 mTorr while the contribution from the double coordinated bond was higher for 50 mTorr. Some peaks assignment for P2p is included in the figure.

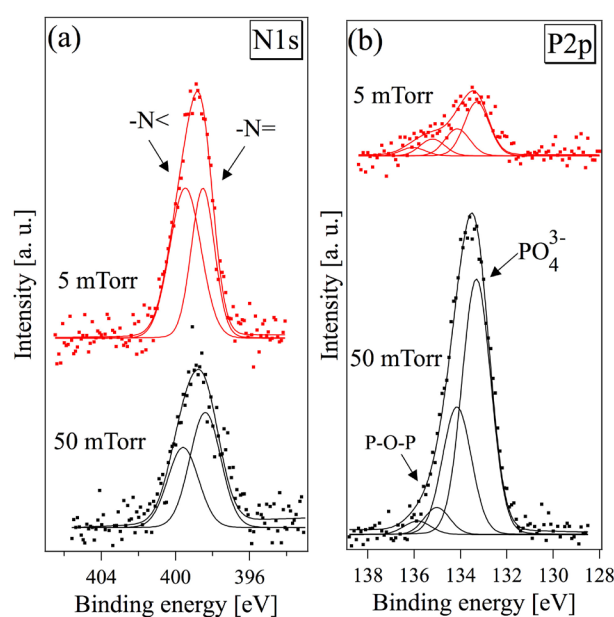


Fig. 2 N1s (a) and P2p (b) peaks by XPS for 5 and 50 mTorr deposited for 100 W in 150 min.

A more detailed investigation of the film structure was not approached in this study due to limited capability to handle the samples in a completely controlled atmosphere after the deposition.

### 3. References

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