



# The role of interface between LiPON solid electrolyte and electrode in inorganic monolithic electrochromic devices

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## ABSTRACT

Transparent lithium phosphorus oxynitride (LiPON) thin films were deposited by RF sputtering at room temperature for electrochromic (EC) applications. We carried out a basic study from single layer, double layers, and eventually to devices. The interactions between LiPON and bottom EC electrode during sputtering were highlighted. The effects of N<sub>2</sub> pressure on structural, morphological, chemical, and electrical properties of the LiPON films were investigated. The Li ionic conductivity of the films increased with decreasing N<sub>2</sub> pressure. The results of Fourier transform infrared spectroscopy and X-ray photoelectron spectroscopy indicated a probable increase of nitrogen content in the films with decreasing N<sub>2</sub> pressure. However, low pressure sputtering process induced the formation of a resistive layer between LiPON and bottom electrode. The electrochemical impedance measurements were conducted to evaluate the charge transfer processes across the interfaces. In the case of WO<sub>3</sub> electrode, the charge transfer resistance at the WO<sub>3</sub>/LiPON interface could be considerably high up to 5100 Ω cm<sup>2</sup>. For the NiO/LiPON interface, the highest value was 1400 Ω cm<sup>2</sup>. The high charge transfer resistance significantly hindered the ion transport, thus leading to irreversible Li insertion/extraction processes and lowered charge capacity in the electrode layers. The cycling reversibility and optical contrast for the complete EC device were compromised accordingly. The device using a 130 nm-thick LiPON ion conductor showed an optical modulation of 40% at 550 nm driven by −1.5 V (coloration) and 1 V (bleaching) with switching time of 30 s.

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## 1. Introduction

Electrochromic (EC) devices have attracted considerable interest from academia and industry due to several promising applications, such as smart windows, non-emissive information displays, variable-reflectance mirrors, and variable-emittance thermal radiators [1–6]. Among these, smart windows for green buildings become a hot research topic because it is closely related to energy saving. The implementation of EC variable-transmittance windows provides a new option for dynamic control of visible light and solar energy.

Electrochromism is based on insertion/extraction of small ions in electrode materials. For smart windows applications, lithium based inorganic all-thin-film structures exhibit plenty of

advantages, e.g., continuous in-line large area manufacturing possibility, no bubble formation, good electrical and physical durability especially under a wide range of temperatures or ultraviolet radiation. Having similar working principles with lithium ion batteries, the Li<sup>+</sup> based devices can change their optical properties dramatically during charging/discharging processes.

The ion conductor layer is one of the core components of an EC device, which is responsible for conducting Li ions and blocking electrons. Finding a suitable inorganic Li ion conductor with high ionic conductivity and high transparency has always been a challenge. As is known for lithium thin film batteries, lithium phosphorus oxynitride (LiPON) has been extensively studied as the solid electrolyte [7]. LiPON presents excellent electrochemical stability with a good ionic conductivity (10<sup>−6</sup> S/cm at room temperature), and the preparation by sputtering is a major advantage [8]. The optical properties of LiPON films have been investigated by Su et al. [9]. The films on silica glass having a transparency higher than 80% in visible region with an optical band gap of 2.94 eV were obtained

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in their study. All these results indicate that LiPON may be a good candidate as ion conductor layer for EC devices. To the best of our knowledge, however, only few studies have been published regarding the application of LiPON in inorganic monolithic EC devices [10,11].

In this paper, transparent LiPON ion conductor layers were prepared under different  $N_2$  pressures by RF sputtering. We observed that low pressure sputtering process resulted in irreversible Li insertion/extraction in NiO or  $WO_3$  electrodes. In order to explain this phenomenon, fundamental electrical and chemical characterizations of LiPON single layer were performed, and electrochemical impedance measurements were carried out to study the solid-solid LiPON/electrode interfaces. In fact, charge transfer resistance at the electrolyte/cathode interface has been widely investigated in solid Li battery systems [12–15]. However, little attention has been focused on the solid-solid electrolyte/electrode interface in monolithic EC devices. In this work, interactions between the upper electrolyte layer and underlying electrode layer during sputtering were noticed. We demonstrated that the solid-solid LiPON/electrode interfaces played an important role in device performance.

## 2. Experimental

### 2.1. Preparation of LiPON thin films

LiPON thin films were deposited by RF reactive sputtering from a  $Li_3PO_4$  ceramic target in pure  $N_2$  atmosphere. ITO-coated glass, silica glass, and Au-coated glass were used as the substrates for different characterizations. The substrates were not intentionally heated nor cooled during the deposition. The  $Li_3PO_4$  target had a diameter of 10 cm and a thickness of 6 mm. The target-to-substrate distance was 15 cm. The chamber was evacuated to a base pressure lower than  $1 \times 10^{-3}$  Pa. Prior to each deposition, the target was pre-sputtered in an argon atmosphere for 20 min in order to remove the surface contaminations. The sputtering power was kept at 300 W (corresponding to a power density of  $3.8 \text{ W/cm}^2$ ). The total  $N_2$  pressure was varied from 0.15 Pa to 2 Pa. The obtained deposition rates of the LiPON films ranged from 0.8 nm/min to 1.8 nm/min. The film thickness was controlled by changing the deposition time. Film uniformity was guaranteed by substrate rotation during the sputtering.

### 2.2. Device fabrication

The configuration of inorganic monolithic EC devices fabricated in this study consisted of  $WO_3$  and NiO as the EC active layers, LiPON as the ion conductor, and two ITO layers as the transparent conductors. All the layers of the devices were deposited by DC or RF sputtering. The deposition of each layer was performed continuously in a multi-target magnetron sputtering system without breaking the vacuum. These conditions are the same for the LiPON-coated NiO and  $WO_3$  double layers. Each target was equipped with a cover to avoid cross contamination. Pre-sputtering took place in pure argon for 20 min before each deposition. The base pressure of

the chamber was evacuated to lower than  $1 \times 10^{-3}$  Pa. The target-to-substrate distance was around 15 cm. ITO-coated glass having a sheet resistance of  $30 \Omega$  and an average transmittance of 85% in the visible region was used as the substrate. No substrate heating was used during the deposition. The sample holder kept rotating to obtain homogeneous thin films. The obtained sheet resistance of the top ITO layer prepared in this work was around 50–60  $\Omega$ . More details on the structure and composition of the NiO and  $WO_3$  layers are given elsewhere [16,17]. Two device configurations were employed according to the deposition sequence of NiO and  $WO_3$  layers, which can be described as Glass/ITO/NiO/LiPON/ $WO_3$ /ITO and Glass/ITO/ $WO_3$ /LiPON/NiO/ITO. The  $N_2$  pressures were varied during depositing LiPON (0.15–2 Pa). The RF power densities for LiPON layers were maintained at  $3.8 \text{ W/cm}^2$ . The thicknesses of LiPON layers were kept at 130 nm. For each condition, 4 samples were prepared in order to guarantee reproducibility. The active size of the device was  $5 \times 5 \text{ cm}^2$ . Detailed sputtering conditions for  $WO_3$ , NiO, and top ITO layers are listed in Table 1.

### 2.3. Characterizations

Electrochemical characterizations were performed on a CHI660E electrochemical workstation (CH Instruments, Inc.). The ionic conductivities of LiPON films were determined by ac impedance measurements. An ac voltage with 100 mV amplitude was applied on the glass/Au/LiPON/Au sandwich structures. The frequency ranged from 1 MHz to 0.1 Hz. The active Au electrode area was  $1 \text{ mm}^2$ . A Zview program was used for fitting the data and the equivalent circuit. The LiPON films with thicknesses ranging from 130 nm to 550 nm were subjected to the tests. The ionic conductivities were found to be basically unchanged regardless of film thickness, which indicates a uniform growth. The LiPON films prepared at various  $N_2$  pressures were measured to evaluate their electrical properties.

The film thicknesses were measured by a stylus profiler (Dektak 6M) and confirmed by cross-sectional scanning electron microscopy (SEM). Film structures were determined by X-ray diffraction (XRD) using a Rigaku D/MAX-2500/PC diffractometer with a Cu  $K\alpha$  source. The Raman measurements on LiPON films were performed using a WITec alpha300R spectrometer with a 532 nm excitation source. Attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR) spectra were acquired using a Nicolet iN10 MX FTIR microscope (Thermo Scientific Inc.). X-ray photoelectron spectroscopy (XPS) measurements were carried out in a VG Scientific ESCALab Mark II photoelectron spectrometer. Spectra were acquired using a monochromatic Al anode. XPS data were analyzed using CasaXPS (Casa Software Ltd.). Peak shifts due to charging were normalized by fixing the C 1s peak to 284.6 eV. The XPS spectra were deconvoluted with a Gaussian-Lorentzian line shape (GL(30)) and a Shirley background. The LiPON samples were preserved in a vacuum-sealed container before XPS measurements. A brief exposure to ambient atmosphere was inevitable. The surface morphologies were observed by an atomic force microscope (AFM, Dimension from Bruker). The atomic ratios of Li/P for LiPON single layer and LiPON-coated NiO or  $WO_3$  double layers were obtained

**Table 1**  
Deposition conditions for the  $WO_3$ , NiO, and top ITO layers of the electrochromic devices.

Film	Target	Power density ( $\text{W/cm}^2$ ) <sup>a</sup>	$O_2/Ar$ (sccm)	Pressure (Pa)	Thickness (nm)	$t_d$ (min) <sup>b</sup>
$WO_3$	W	DC, 3.5	10/30	2	400	10
NiO	Ni	DC, 3.8	6/94	3	200	15
ITO	ITO	DC, 2.5	1/99	0.3	250	20

<sup>a</sup> DC refers to direct current power source.

<sup>b</sup>  $t_d$  stands for deposition time.

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