Fabrication of Atmospherically Stable Lithium-ion Conductive Thin Film Nanoionic Devices

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Program: Global Quantum Leap International Research Training Experience (IRTE)

Funding: NSF AccelNet Program via OISE-2020174

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Abstract:

Modern machine learning's high energy consumption necessitates efficient computing paradigms. Ion-gated nanoionic devices, utilizing lithium-ion conductive electrolytes, offer a highly promising solution via physical reservoir computing. These structurally simple systems control electrical properties, such as synaptic plasticity for neuromorphic applications, through internal ion movement, notably Electric Double Layer (EDL)-mediated carrier doping. This research details the fabrication of these lithium-ion electrolyte devices, characterizing their electrical and optical properties. Crucially, we address the common limitation of high-performance neuromorphic devices, such as all-solid-state transistors, which often lack stability in ambient air.

Summary of Research:

Our study focused on using the solid-state electrolyte $Li_{1.4}$ $La_{0.4}$ $Ti_{1.6}$ $(PO4\ )_3$ (LATP) for neuromorphic AI devices. LATP was selected because it allows for significant in situ manipulation of physical properties via Li-ion conductive electrolytes. Specifically, LATP exhibits high ionic conductivity (~10^{-4} S/cm) and remarkable atmospheric stability. High ionic conductivity LATP thin films are essential for ionic devices operating in an ambient atmosphere due to their atmosphere-independent ionic conductivity and wide electrochemical window.

To deposit the thin films, we utilized the radio-frequency (RF) sputtering technique, where an RF voltage is applied to the target material within a vacuum chamber to generate plasma. LATP was used as the target material and deposited on a SiO_2 (silicon oxide) substrate. Platinum (Pt) was used as the target material for the deposition of the electrodes. For the active channel layer, Indium Tin Oxide (ITO), a transparent semiconductor, was deposited onto a glass substrate via RF sputtering. ITO was chosen for its high electrical conductivity and optical transparency.

We examined the temperature dependence of the resistivity of the LATP thin film, shown in Figure 2. The increase in impedance observed in the low-frequency region of the plot indicates blocking of ions at the metal electrode, confirming that the LATP thin film exhibits ionic conduction. Furthermore, the LATP ionic conductor demonstrated thermally active electrical characteristics, where the electrical resistance decreases with increasing temperature. This behavior, similar to the temperature dependence of electrical resistance in semiconductors, is attributed to the fact that lithium ions move more easily as temperature increases. This mechanism results in an exponential decrease in electrical resistance with temperature. The deposition conditions that yielded the lowest resistivity were identified as the optimal conditions in this study.

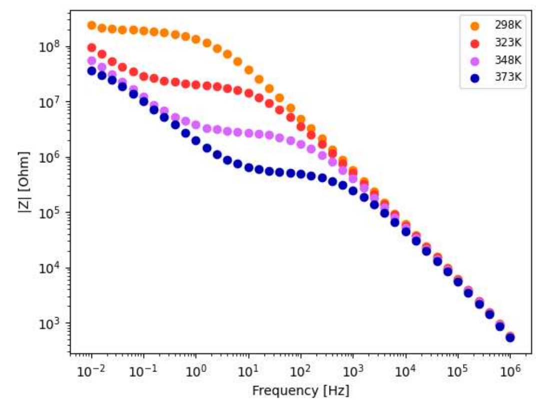

Figure 2: Temperature dependence of impendence against frequency. Deposition conditions: RF 50W, At 8.5 sccm, O2: 1.5 sccm, Deposition time: 4 hours.

The crystallinity of the ITO films on the glass substrate was assessed via X-ray diffraction. The peak intensity was found to increase proportionally with the applied RF power. The thickness of the ITO thin films was measured using a Scanning Electron Microscope as seen in Figure 1, to calculate the deposition rate. Film thicknesses for the samples ranged from 333 nm to approximately 625 nm. A linear relationship between RF power and deposition rate was observed. However, the introduction of oxygen during sputtering caused the deposition rate to decrease, which is likely due to the scattering of sputtered particles by O_2 molecules.

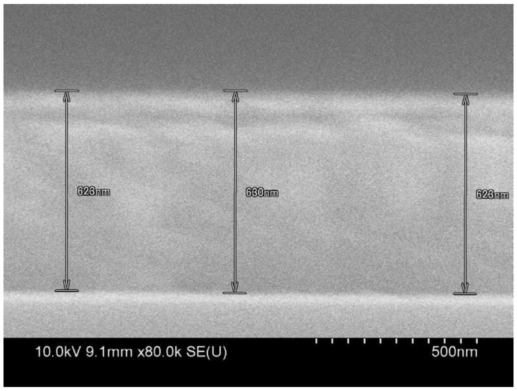

Figure 1: SEM image of thin film. Deposition conditions: RF 75W, Ar 10 sccm, 45 minute deposition time.

The transmittance spectra of the ITO thin films were also measured. ITO is generally transparent at wavelengths above 300 nm, and all fabricated films showed good transmittance, albeit with some variation. This variation is hypothesized to be due to differences in crystallinity resulting from varying RF power and differences in the amount of oxygen incorporated into the ITO thin film. The introduction of oxygen caused the absorption wavelength to become shorter, which indicates a broadening of the band gap.

The LATP-based nanoionic device was fabricated on a Lithium ion Conductive Glass-Ceramic (LiCGC) substrate. As shown in Figure 3, the device structure features a thin film of Pt at the bottom acting as the gate electrode. The ITO thin film, serving as the channel layer, was deposited to a thickness of 30 nm based on the calculated deposition rate for various sputtering conditions. The source and drain electrodes were constructed using a thin film stack of an adhesive Titanium layer followed by a Pt layer. The equivalent circuit for the nanoionic device consists of a parallel RC circuit representing the LiCGC substrate, connected in series with two resistors: one for the ITO thin film and one for the Pt electrodes. The resistance of the Pt electrodes is considered negligible due to its small magnitude.

Initial device characteristics were verified in a vacuum environment (Figure 4), which is the typical operating environment for ionic devices utilizing Li-ion conductive electrolytes. As the gate voltage (VG)

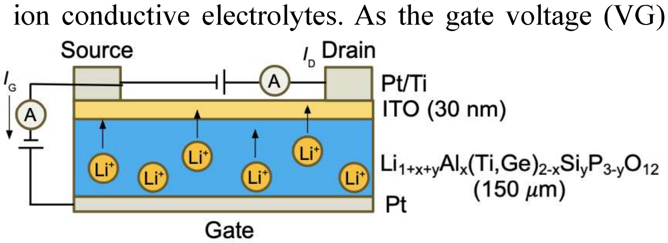

Figure 3: 2D Schematic of Nanoionic Device

was increased from 0 V to 2 V, lithium ions migrated to the ITO side, leading to electron doping to maintain electrical neutrality. These introduced electrons acted as conduction carriers in the ITO channel, resulting in a larger drain current. After the vacuum measurements, the chamber was vented to the ambient atmosphere, and the device characteristics were measured again. A modulation of the drain current with respect to the gate voltage was still observed. However, the overall current amplification was smaller compared to the vacuum measurement. This is attributed to the retention of Li ions in the ITO thin film following the initial VG sweep. Significantly, the devices were left exposed to air for 18 hours after the measurement. A subsequent VG sweep successfully amplified the drain current, conclusively demonstrating effective device operation in air. Hysteresis was observed, with the 50 W, 75 W, and 100 W samples crossing at approximately 1.3 V. This behavior is due to the drain current change during the VG sweep from 2 V to 0 V exhibiting a faster response than the sweep from 0 V to 2 V.

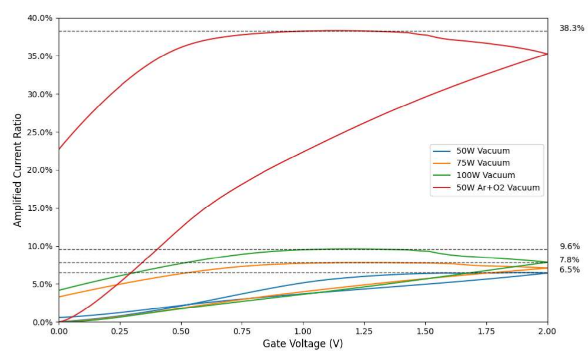

Figure 4: Transistor gate voltage sweep in vacuum.

Conclusions and Future Steps:

Our findings demonstrate that when an ITO thin film is employed as the channel layer, the nanoionic device exhibits good electrical properties in both vacuum and ambient air. Thus, the fabricated LATP-based nanoionic device shows promising stability in ambient air, addressing a major limitation of many existing neuromorphic devices.

Future research will involve further investigation into the optical properties of the nanoionic device and characterization of device performance after prolonged exposure to ambient air.

References:

[1] T. Tsuchiya, D. Nishioka, W. Namiki, K. Terabe, Physical Reservoir Computing Utilizing Ion-Gating Transistors Operating in Electric Double Layer and Redox Mechanisms. Adv. Electron. Mater. 2024, 10, 2400625. https://doi.org/10.1002/aelm.202400625