Sputter-Deposited Amorphous Li₃PO₄ Solid Electrolyte Films

Tsuyoshi Ohnishi* and Kazunori Takada

ABSTRACT: This paper reports the thin-film synthesis of Li₃PO₄ solid electrolytes by RF magnetron sputtering. A relatively high ionic conductivity of more than 1 × 10⁻⁶ S cm⁻¹ is achieved. It is revealed that the crystallization of Li₃PO₄ impedes ionic conduction, and a moderate amount of O₂ addition to Ar suppresses the crystallization and guarantees long-term deposition. Another important finding in this study is that when Li₃PO₄ is deposited on a LiCoO₂ film to construct a thin-film battery, the LiCoO₂ film can be damaged depending on the substrate bias potential relative to the cathode potential propagated through the sputtering plasma. Active control of the bias potential to avoid the damage realizes negligible interface resistance in the thin-film battery.

INTRODUCTION

Solid-state Li-ion batteries are promising next-generation power supplies to replace current Li-ion batteries because of their superior features such as high energy density, long cycle life, and safety. However, it is reported that the interface between a cathode material and a solid electrolyte in a solid-state battery can be rate-determining and thus governs the power density. Converting solid-state batteries into the thin-film form is an effective way to investigate the interface properties since it simplifies the geometry and provides important information about the interfaces.

Lithium phosphorus oxynitride (LiPON) is widely used as a solid electrolyte layer in thin-film batteries because of its relatively high ionic conductivity (∼3 × 10⁻⁶ S cm⁻¹). LiPON was first developed by Bates et al. by sputtering a Li₃PO₄ target in pure N₂. Their Li/LiPON/LiCoO₂ thin-film batteries operate for more than 30,000 cycles with a capacity fading of less than 5%. Since then, a number of thin-film batteries with LiPON have been reported. However, recent first-principles calculations indicate that LiPON is not thermodynamically stable, but kinetically stabilized, upon contact with Li metal and LiCoO₂, and the calculation results are consistent with experimental results. Although partial replacement of O with N (and Li uptake) improves the ionic conductivity, and the conductivity reaches 6.4 × 10⁻⁶ S cm⁻¹ with simultaneous Li enrichment in the target, the incorporation of N into Li₃PO₄ narrows its electrochemical stability window according to the aforementioned calculations.

Li₃PO₄ itself is also used as a solid electrolyte layer in thin-film batteries. Bates et al. examined it along with LiPON by sputtering a Li₃PO₄ target with 40% O₃ in Ar. However, the conductivities of their Li₃PO₄ films were as low as 7 × 10⁻⁹ S cm⁻¹, another group also reported similar values, and in both of these studies, Li₃PO₄ films were deposited by radio-frequency (RF) magnetron sputtering. Meanwhile, Li₃PO₄ films prepared by pulsed laser deposition (PLD) using a high-photon-energy ArF excimer laser showed a relatively higher ionic conductivity of ∼5 × 10⁻⁷ S cm⁻¹, and thin-film batteries made with the PLD Li₃PO₄ operate rather well.

Here, we report the Li₃PO₄ solid electrolyte film synthesis by RF magnetron sputtering with a much improved ionic conductivity. Although there are difficulties in LiPON synthesis in terms of controlling the amount of N incorporated and the simultaneous Li addition to achieve charge neutrality, Li₃PO₄ synthesis is much simpler. We also report thin-film batteries constructed by depositing Li anodes and Li₃PO₄ on LiCoO₂ epitaxial thin films.

RESULTS AND DISCUSSION

A schematic configuration of our specially designed RF magnetron sputtering system is shown in Figure 1. Since multiple sputter cathodes with 2″-diameter targets are equipped, each cathode is oriented to the center of a 2″-diameter substrate holder with a 60° incident angle. The substrate holder is continuously rotated during deposition, and...
10 mm square or 10 mm diameter substrates are located around the middle radius position of the 2° inconel holder for simultaneous multiple deposition. Ar as well as O\textsubscript{2} gases can be introduced through mass flow controllers. The chamber is evacuated by a turbo molecular pump, and a conductance-controllable gate valve is equipped between the chamber and the pump to adjust the chamber pressure independent of the controllable gate valve. Ar as well as O\textsubscript{2} gases can be simultaneously multiple deposition. Ar as well as O\textsubscript{2} gases can be introduced through a low-pass filter during RF sputtering.

**Figure 1.** Schematic configuration of a specially designed RF magnetron sputtering system.

**Figure 2.** Left panels: \(T_{\text{sub}}\) dependences of the film deposition rate (top) and ionic conductivity (bottom). Lines are visual guides. Right panel: \(T_{\text{sub}}\) dependence of GIXRD patterns of 2 h-deposited Li\textsubscript{3}PO\textsubscript{4} films on mirror-polished stainless steel substrates. The 10 mm square and 0.5 mm-thick stainless steel substrate, which works as the bottom blocking electrode, was vacuum-annealed before use to remove the insulative oxidation layer on the surface. The deposition rate was evaluated by the deposition rate, i.e., the film thickness, is almost constant and independent of \(T_{\text{sub}}\) but the ionic conductivity is sensitive to \(T_{\text{sub}}\); a higher \(T_{\text{sub}}\) results in lower conductivity. According to the GIXRD results, when \(T_{\text{sub}}\) is lower than 150 °C, the Li\textsubscript{3}PO\textsubscript{4} film is in an amorphous state, showing a halo centered at \(2\theta = 23°\). On the other hand, when \(T_{\text{sub}}\) is higher, sharp diffraction peaks appear, which correspond to the Li\textsubscript{3}PO\textsubscript{4} crystal phase, and at 300 °C, additional peaks at \(2\theta \approx 14°\) and 28° appear, which are attributable to the Li\textsubscript{3}P\textsubscript{2}O\textsubscript{7} crystal phase. Because the \(T_{\text{sub}}\) at the starting of crystallization coincides well with that during the conductivity drop, it is concluded that the crystallization of Li\textsubscript{3}PO\textsubscript{4} impedes ionic conduction, and an amorphous state is essential for high ionic conductivity. The activation energy estimated from the temperature dependence of ionic conductivity of the amorphous films in the range of 200–350 K was 0.53–0.55 eV. The obtained activation energy and frequency dependence of the impedance were similar to those reported for a PLD-deposited film under an O\textsubscript{2} atmosphere (0.58 eV),\textsuperscript{11} but quite different from that of a RF-sputtered film deposited under pure Ar (0.38 eV).\textsuperscript{7}
suggesting the importance of O₂ introduction. Although low T_{sub} is preferable to make the films amorphous, the substrate is heated up by sputtering plasma during much longer deposition processes, resulting in an unstable T_{sub} in our deposition system, because it does not have a substrate cooler. Heating at moderate temperatures between 50 and 150 °C is reliable to keep T_{sub} constant throughout the deposition and to deposit amorphous films. Although the 200 W data show higher deposition rates (almost double), the higher cathode power tends to damage the target surface severely and quickly (e.g., by causing cracking and color change); thus, a lower RF power is preferred for long-term deposition.

Figure 3 shows the T_{sub} dependence of the mixing ratio of O₂ and Ar gases, in the same manner as in Figure 2, under a total pressure of 0.6 Pa, which was controlled by the conductance valve. According to the results of Figure 2, a T_{sub} of 100 °C is selected, and the room-temperature deposition is also examined without O₂ introduction. It is obvious that the deposition rate is higher when none or a small amount of O₂ is introduced. However, the ionic conductivity is low (less than 10⁻⁶ S cm⁻¹) when no O₂ is introduced. GIXRD results indicate that Li₃PO₄ is crystallized clearly when the O₂ ratio is 1% or less and only slightly when it is 50%. The latter conditions seem similar to those examined by Bates et al. reporting low conductivity; thus, it can be concluded that O₂ is necessary to avoid crystallization; however, excess of O₂ also results in crystallization and decreases the conductivity. In addition, a thin film deposited at room temperature reveals the importance of O₂ introduction. The Bragg peaks indicating crystallization are observed for the thin film deposited without O₂ introduction, even though the film is deposited without substrate heating, and the film shows low ionic conductivity. It means that O₂ gas is anyway needed to suppress the crystallization of Li₃PO₄. Because sputtering is a vacuum process and the deposited films are oxides, the films tend to become oxygen-deficient. In the field of thin-film growth of high Tₘₜ superconducting and other functional oxides, it is well-known that the melting point (T_{melt}) and crystallization temperature of oxide materials tend to be lowered when oxygen is deficient, and thus, high-crystallinity thin films of oxide materials with high T_{melt} can be obtained via a vacuum process, e.g., molecular beam epitaxy and PLD, under much lower T_{sub} relative to their T_{melt} values. Besides, oxygen deficiency is introduced not only in the deposited films but also in the sputtering target, resulting in serious target damage. O₂ gas introduction is therefore necessary to suppress film crystallization and to avoid target damage in the long-term deposition for a thick solid electrolyte layer. O₂ introduction

Figure 3. Left panels: O₂ and Ar gas ratio dependences of the film deposition rate (top) and ionic conductivity (bottom). Lines are visual guides. Right panel: the same dependence of GIXRD patterns of 2 h-deposited Li₃PO₄ films on stainless steel substrates with an incident angle of 0.25°. Deposition conditions are as follows: T_{sub} $100$ °C; RF power, 150 W; total pressure, 0.6 Pa; target–substrate distance, 150 mm; and substrate bias potential, +0.5 V.

Figure 4. Left panels: thickness dependences of the film deposition rate (top) and ionic conductivity (bottom). Lines are visual guides. Right panel: deposited thickness dependence of AC impedance Nyquist plots. Deposition conditions were as follows: T_{sub} $100$ °C; RF power, 150 W; Ar, 20 sccm; O₂, 1 sccm; total pressure, 0.6 Pa; target–substrate distance, 150 mm; and substrate bias potential, +0.5 V. The AC impedance data were taken in the frequency range of $5 \times 10^5$–0.01 Hz with an AC amplitude of 20 mV.
also makes the deposited films stable in air; otherwise, the transparent films devitrify after long-term storage in air, probably because of the humidity.

Figure 4 shows the film thickness dependence of the deposition rate, ionic conductivity, and AC impedance Nyquist plots. Deposition conditions are as follows: $T_{\text{sub}}$, 100 °C; RF power, 120 W; Ar, 20 sccm; O$_2$, 7 sccm; total pressure, 0.6 Pa; and target–substrate distance, 150 mm. XRD patterns before Li$_3$PO$_4$ deposition are also shown in blue curves, and the LiCoO$_2$ thickness is given on the right top of each panel. Right panels are magnified views around LiCoO$_2$ 003 in a linear intensity scale at potentials of 0.0, −1.0, and −2.0 V. Diffraction peaks marked by * in the left top panel indicate the O1 phase 00l.

Figure 5. Red curves: $2\theta$–$\omega$ scan XRD patterns of 15 h Li$_3$PO$_4$-deposited (2–2.5 μm thick) LiCoO$_2$ thin films under different substrate bias potentials during sputtering. Deposition conditions were as follows: $T_{\text{sub}}$, 100 °C; RF power, 120 W; Ar, 20 sccm; O$_2$, 7 sccm; total pressure, 0.6 Pa; and target–substrate distance, 150 mm. XRD patterns before Li$_3$PO$_4$ deposition are also shown in blue curves, and the LiCoO$_2$ thickness is given on the right top of each panel. Right panels are magnified views around LiCoO$_2$ 003 in a linear intensity scale at potentials of 0.0, −1.0, and −2.0 V. Diffraction peaks marked by * in the left top panel indicate the O1 phase 00l.

Damage to the Underlying LiCoO$_2$ Film in Battery Devices. Li$_3$PO$_4$ films were deposited on PLD-grown epitaxial LiCoO$_2$ thin films. The substrates were 0.5 wt % Nb-doped SrTiO$_3$ (111) single crystals with a 10 mm square or 10 mm diameter and 0.5 mm thickness, and LiCoO$_2$ grown in the c-axis orientation with a thickness of 100–200 nm. Details of the LiCoO$_2$ thin-film synthesis are described elsewhere.\textsuperscript{16,17} Figure 5 shows the $2\theta$–$\omega$ scan XRD patterns of 15 h Li$_3$PO$_4$-deposited (2–2.5 μm thick) LiCoO$_2$ thin films under different substrate bias potentials during sputtering. Diffraction patterns before Li$_3$PO$_4$ deposition are also shown in blue curves. Deposition conditions were as follows: $T_{\text{sub}}$, 100 °C; RF power, 120 W; Ar, 20 sccm; O$_2$, 7 sccm; and total pressure, 0.6 Pa. Because the deposition rate of Li$_3$PO$_4$ was stable under certain conditions, the deposited thickness was controlled by the deposition time. It is obvious that there is a clear substrate bias potential dependence of LiCoO$_2$ crystallinity after Li$_3$PO$_4$ deposition. When the potential is lower than −3 V or higher than +0.5 V, LiCoO$_2$ diffraction peaks disappear or the intensity decreases drastically, i.e., the LiCoO$_2$ crystal lattice is destroyed. Besides, it seems that there is an optimal substrate potential, and −2.0 V is close to the optimal value in these depositions as the intensity decrease of LiCoO$_2$ diffraction is minimal. It should be noted here that the conductivity of Li$_3$PO$_4$ films deposited on stainless steel substrates within this potential range is almost constant ($\approx$1.2 × 10$^{-6}$ S cm$^{-1}$), independent of the substrate bias potential.

It appears that an optimal substrate bias potential exists; however, it is not constant but varies gradually with each deposition. Figure 6 shows a plot of the cathode potential when the RF power is set at 100 W before each 5 h deposition. Other deposition conditions were as follows: Ar, 20 sccm; O$_2$, 10 sccm; total pressure, 0.8 or 1.0 Pa; and the target–substrate distance was shortened to 95 mm from and after this experiment to approximately double the deposition rate. The target was changed between depositions #525 and #526. The target change alters the various deposition conditions, but the biggest change is in the DC cathode potential during RF
sputtering. When the target is being worn out, the cathode potential increases and reaches around $-250$ V under these conditions, and finally, the rear indium bond and Cu backing plate appear around the eroding part of the Li$_3$PO$_4$ target. In the case of a new target, the cathode potential is as low as around $-400$ V. Scattering of the cathode potential is mainly caused by the total pressure change. It should also be noted that the total pressure is related to the deposition rate as well as the shutter potential when the pressure is increased in the range of 0.6–1.0 Pa, the deposition rate slightly decreases mainly due to stronger gas scattering, and the shutter potential increases and approaches 0 V. It should be noted that the cathode potential has a strong correlation to the shutter potential around the substrate position as shown in Figure 6 (top). Although the shutter potential is always negative, it changes and correlates to the cathode potential. It can be assumed that the optimal substrate bias potential that preserves the LiCoO$_2$ crystal quality after the Li$_3$PO$_4$ deposition is related to the cathode potential, and it changes gradually with the change in the target surface state.

The change in the optimum bias potential can be seen in Figure 7. It shows 2θ–ω scan XRD patterns of two 15 h Li$_3$PO$_4$-deposited LiCoO$_2$ thin films under the same substrate bias potential of $-0.5$ V, but before and after the target change. Other deposition conditions were as follows: $T_{\text{sub}}$, 100 °C; RF power, 100 W; Ar, 20 sccm; O$_2$, 10 sccm; and total pressure, 0.6 Pa. Between the two depositions, the Li$_3$PO$_4$ target was changed for a new one because the target was worn out. The LiCoO$_2$ crystallinity of the top one is almost preserved, whereas that of the bottom one is degraded severely. It means that the optimal substrate bias potential was around $-0.5$ V, but it has shifted after the target change. Thin-film batteries made by ~500 nm-thick Li anode deposition with vacuum thermal evaporation on Li$_3$PO$_4$ films support the tendency; an open-circuit voltage (ocv) of the thin-film battery with the top sample just after cell construction was 3.9 V, whereas that of the bottom one was 4.3 V.

Here, we discuss what happens when the substrate bias potential is not optimal. Because Li$_3$PO$_4$ and LiCoO$_2$ do not react with each other at substrate temperatures as low as 100 °C, there must be other reasons that relate to the potential. In a battery, the LiCoO$_2$ cathode can be damaged by over-charging and over-discharging, with too high and too low cutoff voltages, respectively. In the sputtering process, the cathode DC potential always becomes negative to sputter the target material by positively ionized Ar gases. Even though it depends on the total pressure, the target–substrate distance, and the on-axis/off-axis geometry, the target and substrate are connected to each other by plasma, which is an electron-conductive gas; thus, the substrate holder is subjected to the cathode potential to some extent, as shown in Figure 6. Since LiCoO$_2$ is underneath the previously deposited Li$_3$PO$_4$ which is connected to the plasma, LiCoO$_2$ can be charged or discharged depending on the substrate bias potential relative to the plasma potential. In Figure 7 (bottom), the LiCoO$_2$ film appears to be overcharged as the X-ray diffraction intensity is considerably decreased, and additional reflections appearing at 2θ $\approx 21.6$ and 44.0° are attributable to the 001 and 002 diffractions of the O1 phase, respectively, which is an overcharged phase of LiCoO$_2$.20,21 Besides, the ocv of the as-constructed battery was 4.3 V, which is higher than the standard charging cutoff voltage of 4.2 V. In Figure 5, the top film is also overcharged, but the bottom one seems over-discharged as LiCoO$_2$ cannot take up extra Li, unlike the LiNi$_{0.5}$Mn$_{1.5}$O$_4$ cathode,16,23 and thus the LiCoO$_2$ crystal collapses.

In the literature, disordered LiCoO$_2$ and Li$_3$MnO$_4$ cathode layers are observed at the interface with LiPON in cross-sectional images obtained by a scanning transmission electron microscope. Although LiPON is deposited by sputtering the Li$_3$PO$_4$ target with pure N$_2$ instead of an Ar and O$_2$ mixture, as in our study, effects of the plasma potential arise likewise: if the substrate potential is not adequate, the cathode layer can be damaged from the LiPON interface. Related to the latter Li$_2$MnO$_4$x the same authors report Li$_3$MnO$_2$ cathode formation from a MnO$_{2-x}$ layer by depositing a LiPON layer on top of it.26 They claim that the LiPON deposition infuses Li ions into MnO$_{2-x}$. Considering the Li$_2$MnO$_4$ disordering and formation of Li$_3$MnO$_4$ from MnO$_{2-x}$ when the substrate potential is lower than that of the...
plasma, discharging (Li-ion infusion) takes place, probably due to the charge build-up of negative plasma by an electronically isolated substrate holder.

The shutter potential can be a good reference to determine the optimal substrate bias potential; however, it is not stable enough for long-term Li3PO4 sputtering, e.g., 10 h deposition; it can shift due to changes in the target surface state, e.g., sudden target cracking, oxygen deficiency introduction, and so on. Therefore, even if the substrate bias potential is determined once from the shutter potential before the deposition, the shift of the plasma potential deviates the substrate bias potential from the optimum value during deposition, which results in low experimental reproducibility. Here, we introduce a strategy to solve the reproducibility problem rather easily. During Li3PO4 deposition, the substrate bias potential is adjusted in real time so that the current meter between the substrate holder and DC power supply (Figure 1) shows zero current. Ideally, no current flows when the substrate bias potential and potential induced from the plasma are balanced. With this active control, we successfully fabricated 10 mm-scale Li/Li3PO4/LiCoO2 thin-film batteries exhibiting high performance; some results have been published already, and another example is described below.

Figure 8 shows our thin-film battery structure and room-temperature performances of the battery in which Li3PO4 (ca. 1.1 μm thick) was deposited under the consideration of the above-described over-charging/discharging processes. Li3PO4 deposition conditions were as follows: Tsub, 50 °C; RF power, 150 W; Ar, 20 sccm; O2, 10 sccm; total pressure, 0.8 Pa; and 5 h deposition. The increased total pressure was to reduce the absolute value of the plasma potential. The RF magnetron sputtering-grown LiCoO2 was a (104)-oriented epitaxial film on a 10 mm square, 0.5 mm-thick 0.5 wt % Nb-doped SrTiO3 (100) substrate, with a film weight of 561 μg (ca. 1.4 μm thick), which was measured with an electronic balance. Details of LiCoO2 sputtering growth are reported elsewhere. Before the Li3PO4 deposition, an ∼100 nm-thick Pt current collector was deposited on a LiCoO2 film by DC magnetron sputtering, which is a 10 mm square film with a circular opening with a diameter of 10 mm,21 and connected to the substrate holder electronically during Li3PO4 deposition. Meanwhile, all of our LiCoO2 films were air-exposed after synthesis for all purposes including weighing, XRD measurement, and Pt deposition. After Li3PO4 deposition, a circular Li anode with a diameter of 8.5 mm was formed above the opening of the Pt current collector.21 Although the LiCoO2 cathode layer was relatively thick, the battery showed a rather high rate capability. Here, a charging/discharging rate of 1 C is defined as 137 mA g−1, which is based on the expected capacity when LiCoO2 is charged up to Li0.5CoO2 at 4.2 V.28 The thin-film battery was charged at a 1 C constant current up to a cutoff voltage of 4.2 V, followed by a constant-voltage charging at 4.2 V for 1 h before each discharge to guarantee a fully charged state. The capacity of low-rate discharge with 7.69 μA (0.1 C) was 108 mAh g−1, whereas the capacity of high-rate discharge with 7.69 mA (100 C) was 60 mAh g−1, maintaining >55% of the low-rate discharge. Figure 8 (bottom) shows a Nyquist plot at the 4.2 V charged state. The semicircle at the higher-frequency region originates from the resistance of Li3PO4 and its ionic conductivity calculated from the x-intercept of the semicircle at a lower frequency is 1.1 × 10−6 S cm−1. It should be noted that other resistances, e.g., the interface resistance between the Li anode and Li3PO4 or Li2PO4 and the LiCoO2 cathode, are not clearly observed, which is different from previously reported results.7,14 Most recently, the reduced interface resistance was reported to be 10.3 Ω cm2 between LiCoO2 and RF-sputtered Li3PO4,29 and also a further reduced resistance of 8.6 Ω cm2 was reported between LiCoO2 and LiPON.7 As the active area of our battery was 0.567 cm2 (8.5 mm-diameter Li anode), at least 15 Ω of interface resistance should appear in the Nyquist plots, if such a resistance exists; however, it cannot be seen in Figure 8 (bottom). The IR drop at 7.69 mA discharge is 1.37 V (Figure 8 middle) and thus R becomes 178 Ω. The resistance of Li3PO4 in Figure 8 (bottom) is 179 Ω, which is almost the same value, i.e., no additional resistance exists, even though the LiCoO2 film is air-exposed. It strongly suggests that the intrinsic interface resistance of Li/Li3PO4 or Li2PO4/LiCoO2 is much smaller than that reported and is almost negligible, and this can be achieved by the active control of the substrate potential during Li3PO4 deposition. In other words, sputtering
or bombardment of high-energy ablated species\textsuperscript{14} during the Li\textsubscript{3}PO\textsubscript{4} deposition has been proposed to cause damages to the LiCoO\textsubscript{2} layer, which results in a large interface resistance, and eliminating these causes lowered the interface resistance to ca. 10 Ω cm\textsuperscript{2}. However, the interface resistance has not reached the intrinsic value yet due to remaining damages under uncontrolled bias potential. In fact, we also observed such an interfacial resistance (\(\geq 10\) Ω cm\textsuperscript{2}) when the bias potential control was not adequate, and the details are reported in a separate paper.

\section*{CONCLUSIONS

This study revealed that RF magnetron sputtering-deposited Li\textsubscript{3}PO\textsubscript{4} can have a relatively high ionic conductivity of more than \(1 \times 10^{-6}\) S cm\textsuperscript{-1}, close to that of LiPON, by avoiding Li\textsubscript{3}PO\textsubscript{4} crystallization; the addition of a certain amount of O\textsubscript{2} gas into Ar as well as a low substrate temperature are effective in suppressing the crystallization. Besides, this study points out the importance of substrate potential control during Li\textsubscript{3}PO\textsubscript{4} deposition on LiCoO\textsubscript{2} films, which has been a hidden, but predominant, process parameter for achieving high performance in thin-film batteries.

\section*{AUTHOR INFORMATION

Corresponding Author
Tsuyoushi Ohnishi — Center for Green Research on Energy and Environmental Materials, National Institute for Materials Science (NIMS), Tsukuba, Ibaraki 305-0044, Japan; orcid.org/0000-0002-2333-7752; Email: ohnishi.tsuyoushi@nims.go.jp

Author
Kazunori Takada — Center for Green Research on Energy and Environmental Materials, National Institute for Materials Science (NIMS), Tsukuba, Ibaraki 305-0044, Japan; orcid.org/0000-0001-7568-1806

Complete contact information is available at: https://pubs.acs.org/10.1021/acsomega.2c02104

Author Contributions
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Notes
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\section*{ABBREVIATIONS

LiPON, lithium phosphorus oxynitride; RF, radiofrequency; PLD, pulsed-laser deposition; \(T_{\text{sub}}\), substrate temperature; XRD, X-ray diffraction; AC, alternating current; GIXRD, grazing-incidence X-ray diffraction; \(T_{\text{melt}}\), melting point; OCV, open circuit voltage

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