LiNbO₃ thin films for all-solid-state electrochromic devices

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ABSTRACT

Lithium niobate (LiNbO₃) thin films were non-reactively deposited onto glass and ITO coated glass substrates by RF magnetron sputtering using a LiNbO₃ target in an argon (Ar) atmosphere at room temperature. The deposition power was 75 W during the deposition process. The optical and electrochromic properties of the LiNbO₃ films with various thicknesses were investigated. Coloration efficiencies and optical modulations of the LiNbO₃ films were investigated for the visible and near infrared region. The amount of inserted/extracted charges into/from the films during the bleaching/coloring process were obtained. The ion conducting and ion storing capabilities of the films were also investigated in detail. The LiNbO₃ film deposited at 20 mTorr with a thickness of 110 nm had both highest optical modulation (20.3%) and coloration efficiency (19.3 cm²/C) at 550 nm. The LiNbO₃ film was used in a unique design all-solid-state electrochromic device. Dry lithiation of the WO₃ film was performed by exposing the film in vacuum to Li vapor atoms, which are given off by RF magnetron sputtering of LiNbO₃. An all-solid-state electrochromic device with a configuration of ITO / NiO / Ta₂O₅ / dry lithiated WO₃ / ITO / glass was fabricated and studied for its electrochromic behavior using a dry-lithiated WO₃ film as an EC layer and an ion source. The optical modulation of the device was 31.4% at 550 nm for the applied potentials of ± 2 V.

1. Introduction

Optical properties of electrochromic (EC) materials such as transmission, absorption and reflection can be reversibly changed when an external potential difference is applied to them. Electrochromatic materials and devices have been developed as an alternative to passive coating materials for light and heat management. The characteristics of EC devices such as low power consumption, high coloration efficiency, memory effects under open circuit conditions make them suitable for use for a variety of applications including architectural “smart” windows, rear-view mirrors and sunroofs for automobiles, information displays, variable-emittance surfaces for temperature control of spacecraft and medical imaging detectors for higher resolution [1–5].

A standard electrochromic device has five superimposed layers (transparent conducting oxide (TCO) layer/cathodic electrochromic layer/ion conducting layer (electrolyte)/anodic electrochromic layer/TCO layer) on one substrate or positioned between two substrates in a laminated configuration. The function of the ion-conducting layer in an EC device is to allow passing across the ions and block the electronic current. For a laminated device, the ion conductor is generally a polymeric electrolyte and the device consists of two half-cells laminated by the polymer. The polymeric electrolytes have better H⁺ and Li⁺ transport capabilities. However, they have a degrading effect on the EC layers and a poor environmental durability. Thus, they cause delamination and shrinkage problems in EC applications [3]. For an all-solid-state EC device, inorganic metal oxide films are used as ion-conducting layers (solid electrolytes) such as LiNbO₃, LiBO₂, ZrO₂, Ta₂O₅, LiBO₄, LiAlF₄, Li₂O-B₂O₃ and Li₂O-CeO₂-SiO₂ [6–19]. Inorganic electrolytes are ideal candidates for device manufacturing without any bubble formation and any sealing problems between the adjacent layers employed in the device. Inorganic films are also highly stable over wide temperature ranges even when they are exposed to UV radiation [19]. Compared to the laminated devices, all-solid-state EC devices have received more attention due to their superior properties like durability and reliability in large area applications, especially [13,19–21]. However, studies on ion conducting materials are still ongoing to improve their ionic conductivity, electronic conductivity and optical transparency. Any electronic current that leaks or passes through the ion-conducting layer serves to short out the applied voltage onto EC layers and blocks the ions flow. A lowered dynamic range, non-uniform coloration and decreased ionic conductivity, increased power consumption and slower switching rates are attributed to the electronic leakage current deteriorating the device performance [22].

The optical properties of electrochromic materials can be changed...
by electron and ion insertion/extraction, depending on the polarity of externally applied potential difference. The liquid or gel electrolyte can be a source of ions used for the bleaching and coloration of EC device. If the ion-conducting layer is a thin-film metal oxide, the ions can be injected into the structure by using wet or dry methods. The thin film metal oxides such as LiNbO$_3$, LiBO$_2$ can also be used as an ion source as well as an ion-conducting layer. In an electrochromic device, ions move between the anodic and cathodic electrochromic layers due to an applied potential difference across transparent conductive layers. Ions may be present in the ion-conducting or electrochromic layer before applying potential difference onto the device. The potential difference creates an electric field between the transparent conductive layers of the device, so positive ions move in the same direction as the electric field. On the other hand, the electrons move in the opposite direction of the electric field and try to arrive at the positively charged transparent conductive layer from the negatively charged transparent conductive layer. Ions and electrons in motion meet at the electrochromic layer and the coloring/bleaching process takes place herein.

In recent years, many studies have focused attention on lithium conductors because of their potential application in such ionic devices as electrochromic displays and thin-film devices [14,15,23]. In Li conductors, LiNbO$_3$ films have high potential to use as a source of ions as well as an ion-conducting layer in EC applications [24,25]. LiNbO$_3$ films have been also used in many applications including non-linear optics, optical modulators and micro-batteries [26–30].

In this paper, we report the electrochromic properties of RF sputtered LiNbO$_3$ films with different thicknesses in detail. In this respect, the ion holding capabilities and ion-conducting properties of the LiNbO$_3$ films were investigated. The LiNbO$_3$ film was deposited onto the WO$_3$ films with various thicknesses to investigate the effects on the dry lithiation behavior of the films during deposition in a vacuum. Finally, a unique design all-solid-state electrochromic device was fabricated with ITO/NiO/Ta$_2$O$_5$/dry lithiated WO$_3$/ITO/glass having a full-cell configuration.

2. Experimental studies

2.1. The deposition of the films

The LiNbO$_3$ thin films were non-reactively deposited on glass substrates by using RF magnetron sputtering at room temperature. The deposition chamber was evacuated to a base pressure of $2.8 \times 10^{-6}$ Torr. The LiNbO$_3$ target (99.9% purity) was 2" (50.8 mm) in diameter and 1/4" (6.35 mm) in thickness. The deposition was performed in an Ar plasma without any reactive gas, the distance between the target and the substrate was 7 cm and the sputtering power was maintained at 40 W. Homogeneity of the films was provided by rotating the substrate holder at a constant speed during the deposition process. Following 10 min of pre-sputtering, the deposition was started by opening the shutter between the target and the substrate holder. The LiNbO$_3$ films were deposited with three different thicknesses (60 nm, 85 nm and 100 nm) at room temperature. In this group, Ar pressure was kept at 20 mTorr.

The LiNbO$_3$ films were deposited on ITO coated glass substrates to perform electrochemical measurements. The ITO films were deposited by using RF magnetron sputtering technique. The deposition was performed in an Ar plasma at 200 °C by using an ITO target. The sputtering power was maintained at 50 W. Their sheet resistances were around 125 $\Omega/\square$ and their optical transmission was approximately 80% in the visible region.

The LiNbO$_3$ thin films were also deposited onto the WO$_3$ films with various thicknesses to investigate the effects on the dry lithiation of the films during deposition in a vacuum. The WO$_3$ films with different thicknesses were deposited onto an ITO coated glass substrates by RF sputtering at room temperature. The tungsten (W) target (99.9% in purity) was 2" (50.8 mm) in diameter and 1/4" (6.35 mm) in thickness. The deposition process was performed in Ar (87.5%) and O$_2$ (12.5%) plasma and the sputtering power was maintained at 40 W. When LiNbO$_3$ was deposited onto the WO$_3$ films using the sputtering technique, spontaneous coloration was observed in the WO$_3$ films. Thus, the WO$_3$ films were dry-lithiated.

Finally, a unique design all-solid-state electrochromic device was fabricated with a full-cell configuration of ITO/NiO/Ta$_2$O$_5$/dry-lithiated WO$_3$/ITO/glass. The deposition parameters of each layer were given in the device section.

2.2. Characterization of the films

The optical transmission and reflection measurements of the films were performed using an Aquila nkd-8000e spectrophotometer over the wavelength range of 350–1050 nm for s- and p-polarized light at an incidence angle of 30°. Film thicknesses were measured by using a quartz crystal monitor during the deposition process.

The crystallographic structures of the films were investigated by using a Rigaku Ultima-IV X-ray diffractometer that used Cu Kα radiation ($\lambda = 0.15418$ nm). The absence of any diffraction peaks related to LiNbO$_3$ in the XRD patterns (not shown) revealed that the films were amorphous.

In order to investigate the electrochromic properties of the films in both half-cell configuration and all-solid-state configuration, a CHI 660C model electrochemical analyzer and a conventional three-electrode cell were used. An Ag/AgCl electrodes and a platinum wire were used as a reference electrode and a counter-electrode, respectively. A 0.01 M solution of LiClO$_4$ in propylene carbonate (PC) was used as an electrolyte. The cyclic voltammetry (CV) measurements of the films were performed with a scan rate of 50 mV/s over the voltage range of ± 2 V at the end of 20th cycle. The corresponding chronocoulometry (CA) measurements of the films were also performed by applying + 2 V and − 2 V with 20 s duration.

The three main parameters are generally used to characterize EC properties of materials. These are optical modulation ($\Delta T$), optical density ($\Delta OD$) and coloration efficiency ($CE$). Optical modulation is the difference between the bleached transmission state and the colored transmission state at a specific wavelength. Coloration efficiency is the ratio of change in optical density ($\Delta OD$) at a specific wavelength in the amount of charge inserted into or extracted from the unit film area:

\[
\Delta T = T_b - T_c \tag{1}
\]

\[
\Delta OD = \log(T_b/T_c) \tag{2}
\]

\[
CE = \Delta OD/\Delta Q \tag{3}
\]

where $T_b$ and $T_c$ are the bleached and colored transmission of the films at a specific wavelength, respectively.

The cathodic and anodic charges were calculated by integrating the negative and positive parts of the CV curves. The areas under the CA negative and positive parts of the CV curves. The areas under the CA negative and positive parts of the CV curves. The areas under the CA negative and positive parts of the CV curves. The areas under the CA negative and positive parts of the CV curves.

The optical absorbance spectra of both bleached and colored state transmissions of the films were measured by using a Hitachi U0800D diode array spectrophotometer over the spectral range of 190–1100 nm at normal incidence during the EC cycles.

The electrochemical impedance spectroscopy (EIS) was used to understand the kinetics of electrochemical reactions at the electrodes. The electrochemical impedance measurements of the LiNbO$_3$ films were performed at 0.05 V over a frequency range of 0.01 Hz–0.2 MHz using a three-electrode system by using a CHI electrochemical analyzer.
3. Results and discussion

3.1. The electrochromic behavior of the LiNbO$_3$ films

The thickness of the solid electrolyte is a key parameter to obtaining a high performance EC device. If the thinner electrolyte layer is used in the device, a short-circuited electrochemical cell establishes because of the shorting between anodic and cathodic EC layer. Electrolyte with greater thickness needs greater voltage to work [31,32]. There is thus a strong need to optimize the layer thickness. The LiNbO$_3$ thin films were deposited at 20 mTorr onto glass and ITO coated glass substrates at room temperature with various thicknesses to investigate the effects on the optical and electrochromic properties. The optical transmissions of the LiNbO$_3$ films deposited with various thicknesses (60 nm, 85 nm and 110 nm) on glass substrates increased from 78% to 86% at 550 nm with increased film thickness. The optical transmission and reflection spectra of LiNbO$_3$ thin films deposited on glass substrates with various thicknesses are seen in Fig. 1. Ion-conducting layers should have high optical transmission for practical applications of electrochromic devices not to deteriorate the overall transparency of the device [13]. Therefore, the deposited LiNbO$_3$ films have a suitable optical transmission to be used as an ion-conducting layer in electrochromic devices.

The cyclic voltammetry and the corresponding chronoamperometry curves at the end of the 20th cycle are given in Fig. 2, respectively. The color of the film changed from transparent to light brown during the cathodic potential scan (from +2 to −2 V) by simultaneous intercalation of electrons and Li$^+$ ions from the electrolyte into the film. The films bleached during the anodic potential scan (from −2 to +2 V) due to the deintercalation of Li$^+$ ion from the films. It is confirmed that the LiNbO$_3$ films showed a cathodic electrochromism.

Injected/extracted charge density of the films were obtained by integrating the area under cyclic voltammetry curves for cathodic and anodic scan, respectively. It was seen that the injected/extracted charges of the films decreased with the increasing film thickness. The film with a thickness of 60 nm had the highest injected/extracted charges.

During the chronoamperometry measurements, the voltage was stepped between the potential of +2 V (coloration) to −2 V (bleaching) with a duration time of 20 s for each potential. The areas under the CA curves decreased with the increasing film thicknesses as it is expected. The films exhibited quite a fast switching response. The electrochromic parameters of the LiNbO$_3$ thin films with different thicknesses are seen in Table 1. The colored and bleached transmission spectra of the LiNbO$_3$ films are shown in Fig. 3. It was observed that the LiNbO$_3$ films deposited with various thicknesses showed reversible electrochromic properties. The coloration efficiency and optical modulation spectra of the films with various thicknesses are illustrated in Fig. 4. The values of CE and ΔT decreased in visible range slightly with increased film thicknesses from 60 nm to 85 nm. Then a drastic increase was observed as the film thickness increased from 85 nm to 110 nm. The highest CE and ΔT were calculated 19.3 cm$^2$/C and 20.3% for the film with a thickness of 110 nm at a wavelength of 550 nm, respectively. The higher CE...
indicates that EC film provide a large optical modulation with a small amount of inserted or extracted ion/charge. Since a small amount of charge insertion or extraction rate enhances the cyclic stability of EC film that is a crucial parameter to construct a durable EC device with a long lifetime [33]. Thus, the LiNbO3 film with a thickness of 110 nm deposited at 20 mTorr was chosen to investigate the effects of dry lithiation process and fabricate the all-solid state EC device. In literature, the optical modulation of the LiNbO3 film deposited using a sol-gel technique by Özer and Lampert was around 5% at 550 nm [34]. The optical modulation of the film was considerably lower even though the films are thicker than that of the film deposited in the current study. The electrochromic properties of the metal-oxide EC layers generally enhance with increasing film thickness [35–37]. As the film thickness increases, the depth of diffusion increases. Thus, the amount of charge transferred is dependent on the thickness of the film during the EC cycling [37].

### 3.2. The ion-conducting behavior of the LiNbO3 films

The electrochemical impedance measurements were carried out at 0.05 V over a frequency range of 0.01 Hz–0.2 MHz to investigate the ion conducting properties of the films. The Nyquist plots for the LiNbO3 thin films deposited on ITO coated glass substrates are shown in Fig. 5. The Nyquist plots in low-frequency region according to the following equation [40]:

$$D = \frac{R T^2}{2 A F n^2 F^4 C^2 \sigma^2}$$  \hspace{1cm} (4)

where $R$ is gas constant, $T$ is absolute temperature, $n$ is number of electron(s) per molecule oxidized, $A$ is surface area, $F$ is Faraday’s constant, $C$ is concentration, $D$ is diffusion coefficient and $\sigma$ is Warburg factor which depends to $Z_w$ as in Eq. (5):

$$Z_w = R_s + R_a + \sigma \omega^{-1/2}$$  \hspace{1cm} (5)

The diffusion coefficients of Li$^+$ ions into the LiNbO3 thin films were determined to be in the range of $10^{-12}$ cm$^2$/s. The highest diffusion coefficient was obtained as $2.79 \times 10^{-12}$ cm$^2$/s for the LiNbO3 film with a thickness of 85 nm. The radius of the semicircle were obtained for the films with thicknesses of 60 nm and 85 nm are slightly different. The film with the thickness of 110 nm had the largest

![Fig. 3. Optical transmission spectra for the colored and bleached states of LiNbO3 films with various thicknesses: a) 60 nm, b) 85 nm, c) 110 nm.](image-url)
obtained as $8.47 \times 10^{-9}$ S/cm for the LiNbO$_3$ film with a thickness of 110 nm.

The time dependence of current of the films with applied potential of $+2$ V is shown in Fig. 6. The current decreases rapidly with time and stabilizes around a specific current value called a leakage current $I_L$. The electronic conductivity is given with Eq. (7):

$$\sigma = \frac{dI}{UdA}$$

where $U$ is the applied voltage, $d$ is the thickness of the film, $A$ is the electrode active area [44]. The electronic conductivity of the LiNbO$_3$ film with a thickness of 110 nm was found to be $1.57 \times 10^{-10}$ S/cm.

The ionic conductivity of the LiNbO$_3$ film deposited by reactive magnetron sputtering with a thickness of 980 nm was reported to be $2 \times 10^{-7}$ S/cm while the diffusion coefficient for Li$^+$ in LiNbO$_3$ was given as $2 \times 10^{-11}$ cm$^2$/s [19].

### 3.3. The dry lithiation process with the LiNbO$_3$ film

WO$_3$ films exhibit a cathodic coloration. Reduction of W atoms from valance 6$^+$ to 5$^+$ plays a vital role to understand the electrochromic coloring/bleaching process observed in WO$_3$ films [45]. Optical properties change when electrons move into WO$_3$ from a transparent conductor along with charge-balancing ions entering from an electrolyte. As-deposited WO$_3$ thin films are generally transparent, however when ions are inserted, their color turns to blue [45]. The following reaction describes the electrochromic process of the WO$_3$ film:

$$\text{WO}_3 + x(A^+ + e^-) \leftrightarrow A_x\text{WO}_3$$

where $A^+$ can be any anions such as H$^+$, Li$^+$ and Na$^+$ [46–48]. Despite the higher diffusion coefficient of hydrogen, which entails a faster optical switch, lithium ions are more stable once incorporated into a WO$_3$/NiO complementary electrochromic device [48]. Lithiation is one of the crucial processes leading to the color change observed in EC materials for the fabrication of all-solid-state electrochromic devices. The color change can be implemented via a wet lithiation technique or a dry lithiation technique. The lithium ions are introduced from liquid/gel electrolyte into the EC layer in wet processes. Wet lithiation have been widely used in EC applications. The evaporated or sputtered Li$^+$ ions are introduced into the EC layer during the thin film deposition in the dry techniques.

In the present work, the LiNbO$_3$ thin film was deposited onto the WO$_3$ thin films with various thicknesses to investigate the effects of the EC layer on the dry lithiation process. The WO$_3$ films were deposited onto ITO coated glass substrates at room temperature by using a tungsten (W) target. The deposition process was performed at 22.5 mTorr in a plasma consisting of Ar and O$_2$ mixture. The sputtering power was maintained at 40 W. The WO$_3$ films were deposited with various thicknesses (30 nm, 150 nm, 215 nm and 350 nm) to investigate the effects on the dry lithiation process. To reach this goal, the LiNbO$_3$ sputtered at 20 mTorr with a thickness of 110 nm was deposited onto the WO$_3$ films. The LiNbO$_3$ film with a thickness of 110 nm was used because of its observed higher electrochromic activity. The LiNbO$_3$ thin
film was non-reactively deposited at room temperature by using a LiNbO₃ target. The sputtering power was maintained at 40 W. When the WO₃ film was exposed by lithium ions in vacuum, their color changed from bleached to deep blue. The colorless as-deposited WO₃ films spontaneously became deep blue in color by sputtering of LiNbO₃ onto them. The origin of the observed coloration of the WO₃ films would be the ejected lithium ions from the sputtered LiNbO₃ target, which might diffuse into the exposed WO₃ films. Similar coloration of WO₃ by dry lithiation has been observed in the case of thermal evaporation of LiNbO₃ powder in a tungsten boat [49] and electron-beam evaporation of Li metal [50] under vacuum.

The optical transmission spectra of the as-deposited WO₃/ITO/glass and dry lithiated WO₃/ITO/glass structures with various thicknesses of WO₃ are shown in Fig. 7. The as-deposited WO₃ films were all colorless. The optical transmission spectra of the lithiated WO₃ films were measured immediately after the films were taken out from the deposition chamber. The WO₃ thin films with four different thicknesses were used in the above-mentioned structures. In the current study, the dry lithiation process was used by magnetron sputtering of the LiNbO₃ onto the active EC layer without cutting the vacuum.

The lithiated WO₃ film with a thickness of 30 nm was found to be light blue, and the optical transmission of the film was 73.4% at a wavelength of 550 nm. When the thickness of the WO₃ layer was increased from 30 nm to 350 nm, the optical transmission of the structures visibly decreased and reached a value of 37.1% at 550 nm. The color change observed from light to dark blue with increase in the WO₃ film thickness. When the thickness of the WO₃ layer was increased from 30 nm to 350 nm, the optical transmission of the films also decreased from 67.3% to 19.5% at 850 nm. In general, ion diffusion occurs by an interstitial mechanism in electrochromic phenomena. Therefore, the depth of diffusion and the electrochromic activity increase with increasing electrochromic layer thickness [37]. In the current study, it is very first time was investigated the lithium insertion into the WO₃ films with various thicknesses deposited by RF magnetron sputtering technique. The dry lithiated WO₃ layer obtained by following a very easy procedure without cutting the deposition process. It was observed that the lithiation degree strongly depends on the thickness of the WO₃ film.

In the articles by Porquieras et al. were focused on the lithium insertion into the WO₃ thin films by thermal reactive evaporation. They showed that higher lithium insertion ratios caused irreversible electrochromic reactions in WO₃ layer. There was a limit at which lithium was inserted irreversibly into the WO₃ layer [24,25,48].

3.4. All-solid-state thin film electrochromic device

The unique design all-solid-state EC device was fabricated with a full-cell configuration of ITO/NiO/Ta₂O₅/LiNbO₃/WO₃/ITO/glass. In the device, ITO film acts as a transparent electrode while NiO film acts as an anodic electrochromic layer, Ta₂O₅ film acts as an ion conducting layer and dry lithiated WO₃ film acts as a cathodic electrochromic layer as well as a source of ions. The device constituted from individual film components, each of which was deposited under optimized deposition
conditions [33]. The deposition parameters of the individual films employed in the all-solid-state EC device are given in Table 2.

For the fabrication of the all-solid-state EC device, the WO3 film was deposited onto ITO coated glass. Afterwards, the LiNbO3 film was deposited on previously WO3 coated ITO glass substrates. The Ta2O5 thin film was deposited on the dry lithiated WO3/ITO/glass structure. Then the NiO as an anodic layer and ITO layer as a top contact electrode were deposited onto the structure, respectively. Thus, the dry lithiation process was used in the all-solid-state EC device. The overall device with an active area of 1.5 × 1.5 cm2 was sealed with transparent epoxy resin to prevent the absorption of moisture from the atmosphere. The schematic diagram of the device was inserted into Fig. 8.

The optical transmission and reflection spectra of the as-deposited all-solid-state EC device are shown in Fig. 9. The optical modulation of the device was about 31.4% (from a colored state of 36.2% to a bleached state of 73.4%) at 550 nm.

Table 2

<table>
<thead>
<tr>
<th>Target</th>
<th>Working pressure (mTorr)</th>
<th>O₂ concentration (%)</th>
<th>RF power (W)</th>
<th>Film thickness (nm)</th>
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</thead>
<tbody>
<tr>
<td>ITO</td>
<td>36</td>
<td>–</td>
<td>50</td>
<td>190</td>
</tr>
<tr>
<td>NiO</td>
<td>15</td>
<td>–</td>
<td>75</td>
<td>290</td>
</tr>
<tr>
<td>Ta₂O₅</td>
<td>40</td>
<td>–</td>
<td>75</td>
<td>230</td>
</tr>
<tr>
<td>LiNbO₃</td>
<td>20</td>
<td>12.5</td>
<td>40</td>
<td>110</td>
</tr>
<tr>
<td>WO₃</td>
<td>20</td>
<td>12.5</td>
<td>40</td>
<td>350</td>
</tr>
</tbody>
</table>

The optical and electrochromic properties of the LiNbO3 films deposited by RF magnetron sputtering were investigated in detail to observe their ability to use in all-solid-state EC devices as a passive electrochromic layer and/or an ion-conducting layer as well as a source of ions.

The electrochromic properties of the LiNbO3 films were exhibited that they acted as a cathodic material. The highest coloration efficiency (19.3 cm²/C) and optical modulation (20.3%) were obtained for the film with a thickness of 110 nm deposited at 20 mTorr.

The optical transmission of the LiNbO3 films deposited onto glass substrates was around 82% in the visible region that is high enough being used as an ion-conducting layer in electrochromic devices. The ionic conductivities of the films were found to be 10⁻⁸ S/cm while the diffusion coefficients for Li⁺ were calculated as in the range of 10⁻¹² cm²/s. The electronic conductivities were around the range of 10⁻¹¹ S/cm.

The dry lithiation of WO3 films were performed by sputtering the LiNbO3 film onto the WO3 layer with various thickness. When the LiNbO3 layers were sputtered onto the WO3 layers in a vacuum, spontaneous coloration of the WO3 layers were observed. Thus, the dry lithiated WO3 films were obtained. The WO3/ITO/glass structure with a thicker WO3 layer (350 nm) had a higher transmission variation by sputtering LiNbO3 onto it. The optical transmission of the structure changed from 73.4% to 37.1% at 550 nm.

Finally, the uniquely designed all-solid state EC device with a sequence of thin films on a single substrate was fabricated by using a RF magnetron sputtering technique. The device configuration in the full-cell structure was ITO/NiO/Ta₂O₅/LiNbO₃/WO3/ITO/glass. The bleached and colored state optical transmission of the device were 67.6% and 36.2% at 550 nm, respectively. The very first time dry lithiated WO3 films by sputtering of LiNbO3 onto it were employed in an all-solid-state EC device in the current study.

The results indicate that the LiNbO3 films are a very promising candidate that not only performs as an electrochromic layer, but also as an ion conducting/ion source layer. They can be easily integrated to in-line industrial manufacturing of state-of-the-art all-solid state electrochromic devices.

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