Journal of Alloys and Compounds 509 (2011) 1910–1914

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: www.elsevier.com/locate/jallcom

Effects of annealing temperature on structure and opt-electric properties of ion-conducting LLTO thin films prepared by RF magnetron sputtering

Yuli Xiong, Haizheng Tao, Jiang Zhao, Hao Cheng, Xiujian Zhao*

Key Laboratory of Silicate Materials Science and Engineering (Wuhan University of Technology), Ministry of Education, Wuhan, Hubei 430070, PR China

ARTICLE INFO

Article history:
Received 15 June 2010
Received in revised form 10 October 2010
Accepted 21 October 2010
Available online 30 October 2010

Keywords:
LLTO thin films
RF magnetron sputtering
Ion-conducting
Annealing temperature

ABSTRACT

Highly transparent and ion-conducting lithium lanthanum titanate (LLTO) thin films were deposited on ITO/glass substrates by RF magnetron sputtering. The results of X-ray diffraction indicate that the as-prepared LLTO thin films and the annealed ones at temperatures up to 300 °C are amorphous; however, crystal phases, including $La_{0.56}Li_{0.33}TiO_3$ and other unexpected ones, appear on the annealed films at 400 °C. SEM and AFM results show that the prepared films turn to be denser, smoother and more uniform up to 300 °C while the deteriorative results come out following the further enhancement of annealing temperature. Further characterization of opt-electric properties of the prepared films reveals that the annealed ones at 300 °C own the best optical transmittance of 85% and the highest room temperature ionic conductivity of 5.25×10^{-5} S cm^{-1}, which are suitable for the application as an electrolyte of all-solid-state electrochromic devices.

1. Introduction

Due to their higher levels of safety and reliability compared with the liquid ones, solid lithium-ion conductors are of major interest because of their potential applications as electrolytes in energy storage devices, electrochemical sensors, and electrochromic devices [1–3]; however, these solids must meet a number of requirements before they become commercially attractive. For example, to obtain an application in an electrochromic device, the following characteristics, such as high room temperature ionic conductivity, high transmittance level in a required spectral range and no corrosion with the adjacent electrochromic materials, must be fulfilled [4].

As a promising lithium ionic conductor, perovskite-type $Li_{3x}La_{2/3-x}TiO_3$ (LLTO) first reported by Inaguma et al. [5,6], whose room temperature ionic conductivity in a bulk form is higher than 10^{-3} S cm^{-1}, attracted much attention these days. Using LLTO in pH sensors, Bohnke et al. did a lot of pioneering work [3,7,8]. Recently, to further improve the ionic conductivity and reveal the conductive mechanism, much investigation on bulk LLTO ceramic electrolytes obtained through different fabricating methods was conducted by the famous group leaded by CW Nan [9–11].

Recently, utilizing tantalum oxide films prepared by reactive dc magnetron sputtering as the electrolyte layer, the electrochromic all-solid-state switchable mirror glass was fabricated, which can switch its optical state between the reflective (mirror) and transparent states [12,13]. We feel LLTO thin films could also be applied in the all-solid-state electrochromic devices. Considering its strongpoint such as high throughput, controllable thickness and good adhesion to substrate [14], magnetron sputtering method was adopted in this work to prepare LLTO thin films. To obtain the optimum optical and electric properties, the detailed investigation on the effects of annealing temperature upon the structure, morphology, optical and electric properties were conducted.

2. Experimental procedures

The $La_{0.56}Li_{0.33}TiO_3$ ceramic target was synthesized by solid-state reaction from La_2O_3 (99.9999%), Li_2CO_3 (99.4%), and TiO_2 (99.1%) powders. A two-step fabricating process was carried out. First, the batch, which was ball-milled using ethanol and zirconia balls for 4 h, were kept at 600 °C for 6 h and 1000 °C for 12 h to expel CO_2 gases. Subsequently, the calcined batch was grounded thoroughly and pressed at 200 MPa for 20 min to obtain a disk with 56 mm in diameter. Then the target was obtained through heating the disk to 1200 °C with a rate of 3 °C min^{-1}, holding the temperature for 8 h then cooling to room temperature with a rate of 5 °C min^{-1}.

Through RF magnetron sputtering method, LLTO thin films were prepared with ITO coated glasses as substrates, which were ultrasonically cleaned in acetone, ethanol and deionized water for 30 min. The distance between target and substrate is 6 cm. Before deposition, the target was pre-sputtered for 10 min to remove any contaminants on the target surface. The base pressure of the deposition system was 1×10^{-3} Pa. During sputtering, the pressure increased to 1 Pa as the mixed gas (70%Ar, 30%O_2) was introduced into the chamber. The sputtering power was 80 W. After deposition, the films were annealed in air at various temperatures from100 to 400 °C for 2 h.

The crystal phases in LLTO target and thin films was determined by X-ray diffraction method (XRD, X'pert PRO XRD, Rigaku Co., Japan) over the angular range $10° < 2\theta < 80°$. The Li/La film composition was evaluated by Inductively Coupled Plasma (ICP) using a Perkin Elmer Optima 4300 DV spectrometer. The film morphology was observed by field-emission scanning electron microscope (FESEM, S-4800,

* Corresponding author. Tel.: +86 27 87652553; fax: +86 27 87669729.
E-mail address: opluse@whut.edu.cn (X. Zhao).

0925-8388/$ – see front matter © 2010 Elsevier B.V. All rights reserved.
doi:10.1016/j.jallcom.2010.10.086

HITACHI, Japan) and atomic force microscopy (AFM, NanoScope (R) IV model, Veeco Metrology Group, USA). The UV–Vis transmittance spectra were recorded with an UV–Vis spectrophotometer (UV1601, SHIMADZU, Japan). AC Impedance measurements for the ionic conductivity of LLTO thin films with sandwich configuration Glass/ITO/LLTO/Al were performed at room temperature (25 °C) in the frequency range from 1 Hz to 1 MHz with an Autolab (HEMIE B.V., ECO, Holland) instrument.

3. Results and discussion

3.1. Structure and morphology of LLTO thin films

XRD patterns of the LLTO target and thin films are shown in Fig. 1. All the diffraction peaks of the target can be ascribed to the reflections of $La_{0.56}Li_{0.33}TiO_3$ crystal phase [1,2], which verified that the fabricating process conducted in this work is appropriate. However, the as-deposited thin films are amorphous, together with the annealing ones at the heat-treated temperatures below 400 °C. Certainly, the $La_{0.56}Li_{0.33}TiO_3$ crystal phase appears when the annealing temperature is higher than 400 °C. At the same time, other unexpected crystal phases such as ITO also come out in the

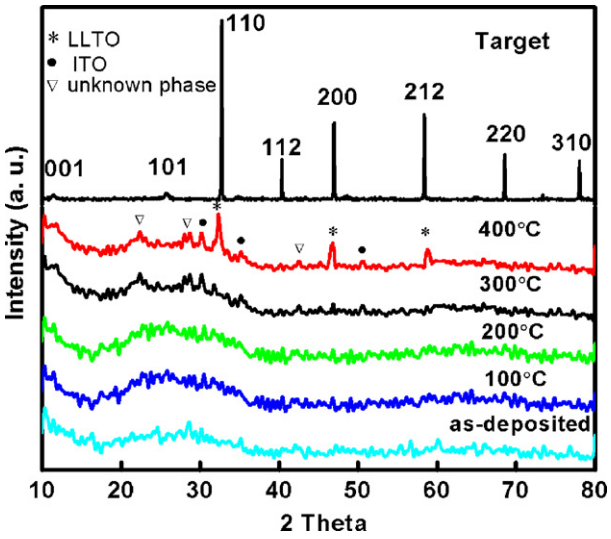

Fig. 1. XRD patterns of LLTO target and thin films annealed at various temperatures.

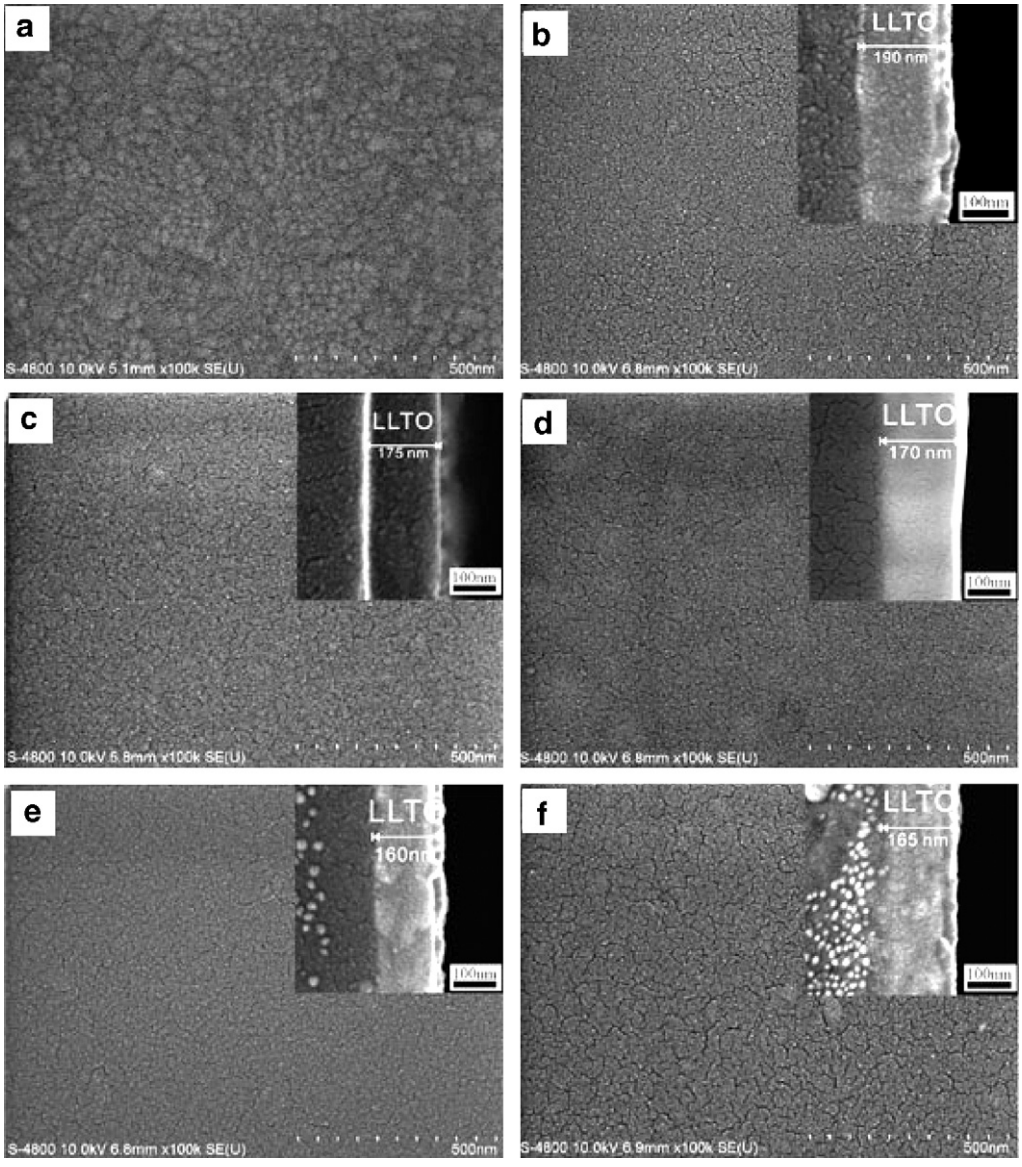

Fig. 2. SEM images of surfaces of (a) ITO/glass substrate, (b) as-deposited LLTO thin film and LLTO thin films annealed at (c) 100 °C, (d) 200 °C, (e) 300 °C and (f) 400 °C together with their corresponding cross-sectional images in the upper right inserted images of (b)–(f).

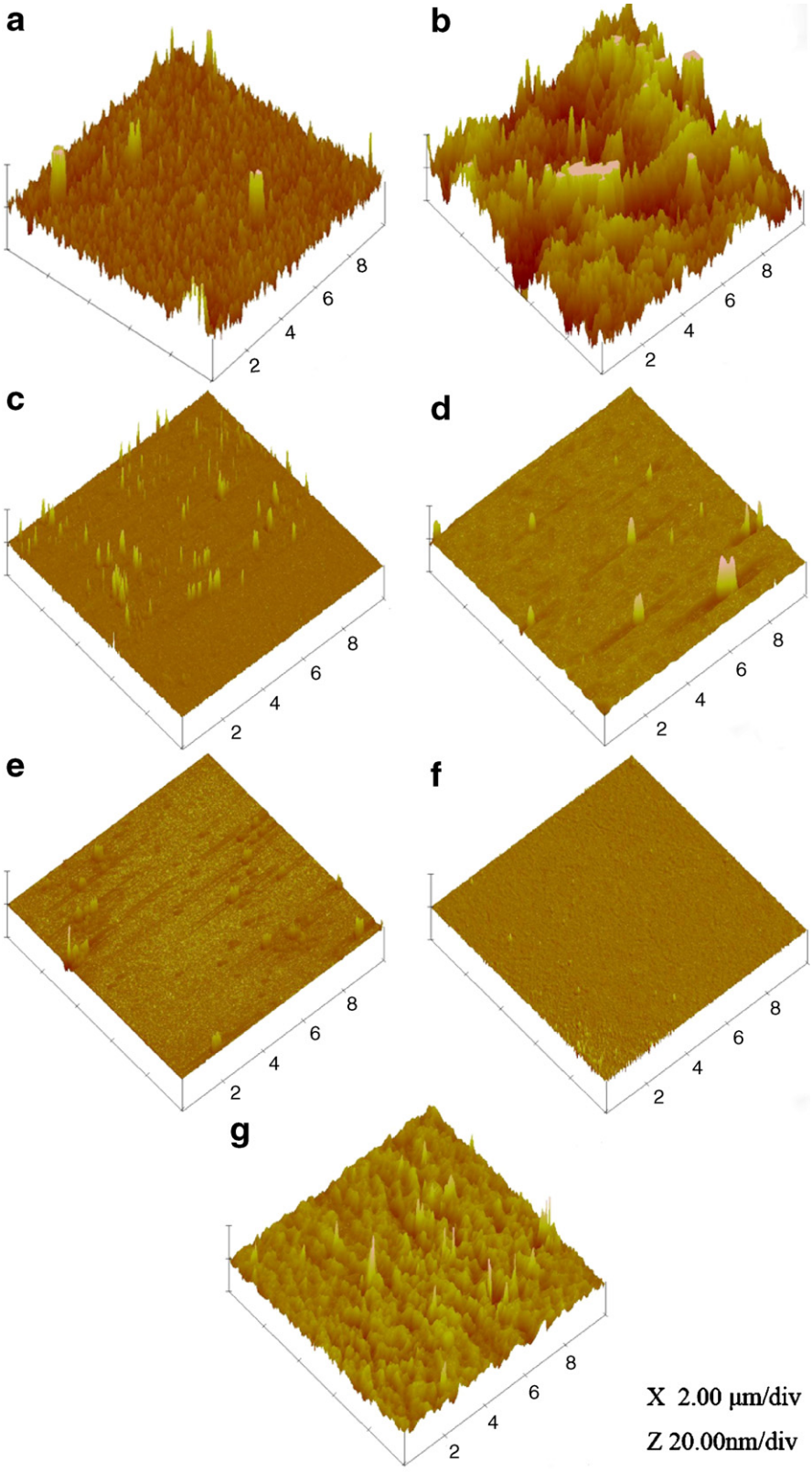

Fig. 3. AFM images of (a) ITO/glass substrate, (b) substrate annealed at 400 °C, (c) as-deposited LLTO thin film and LLTO thin films annealed at (d) 100 °C, (e) 200 °C, (f) 300 °C and (g) 400 °C.

400 °C annealed samples as shown in Fig. 1, whose origin is not so clear at the present time.

As shown in the images of surfaces in Fig. 2, the morphology of the substrate (Fig. 2a) is a little different from that of LLTO thin films (Fig. 2b–f). Compared with that of substrate, the surfaces of LLTO thin films are very smooth, dense, and uniform, which is very important for thin film electrolytes to avoid shortcut and safety problems. In addition, from the cross sectional images of LLTO thin

Table 1
Ionic conductivity at room temperature, pre-exponential factor and activation energy of LLTO thin films annealed at various temperatures.

LLTO film sample	σ (S cm^{-1})	σ_0 (K S cm^{-1})	Ea (eV)
As-deposited	0.71×10^{-5}	1.75×10^{3}	0.35
Annealed at 100 °C	1.50×10^{-5}	3.71×10^{3}	0.35
Annealed at 200 °C	3.72×10^{-5}	9.19×10^{3}	0.35
Annealed at 300 °C	5.25×10^{-5}	12.97×10^{3}	0.35

films shown in the insert graphs in Fig. 2, we can deduce that the coalescence of LLTO thin films and substrate is very tight and the thickness of films decreases with the enhancement of annealing temperature from 100 to 300 °C except for the slight expansion annealed at 400 °C. Finally, some important change occurs about the morphology of ITO layer for the films annealed at a temperature of 400 °C, which is coincident with the results of XRD patterns.

To further characterize the morphological features, AFM images of thin films and substrate are present in Fig. 3. The clear decrease of surface RMS (roughness mean square) of LLTO thin films following the enhancement of annealing temperature up to 300 °C from 1.236 to 0.321 nm can be obtained from Fig. 3c to e, which indicate the increasing smooth degree of the corresponding films. This fattening effect of films through proper annealing process maybe originated from more uniform and denser distribution of ions explained by the reference [15]. In addition, through the comparison of images of substrate before and after annealed at 400 °C for 2 h (Fig. 3a and b), we can clearly see that the process of annealing higher than 400 °C had a deleterious effect on the morphology, which is further verified by the image of the LLTO film annealed at 400 °C (Fig. 3g). In fact, the above mentioned effect was reported before in the reference [16], which indicted that the annealing at 400 °C of ITO glass substrates would induce a harmful change of physical and chemical properties. Therefore, the films annealed at 400 °C will not be further discussed in the following sections.

3.2. Ionic conductivity

According to the report of Inaguma et al. [17], on the complex impedance spectra of LLTO ceramic materials, there exists two semi-circles which ascribed to the bulk part and grain boundary part respectively. However, as shown in Fig. 4, a complete single semicircle within the measured frequency range appears for the as-prepared and annealed films similar with the results of refs. [18,19], due to the absence of perfect crystal grains and the amorphous nature of obtained films which can be confirmed by the above mentioned XRD results.

The ionic conductivity was calculated according to the following equation.

$$\sigma = \frac{d}{(R \times A)} \quad (1)$$

where d is the electrolyte thickness, A the electrode area and R the electrolyte resistance. The calculated ionic conductivities of LLTO thin films, which increase from 0.71×10^{-5} S cm^{-1} of the as-prepared film to 5.25×10^{-5} of the film annealed at 400 °C, are shown in Table 1.

Temperature dependence of ionic conductivity of the LLTO thin films are shown in Fig. 5, which confirm that thermally activated ionic conduction is the main conductive mechanism of the prepared LLTO thin films considering the facts of gradual enhancement of conductivity following the increase of temperature [20].

Using the following Arrhenius equation:

$$\sigma = \frac{\sigma_0}{T} \exp\left(\frac{-\mathrm{Ea}}{kT}\right) \quad (2)$$

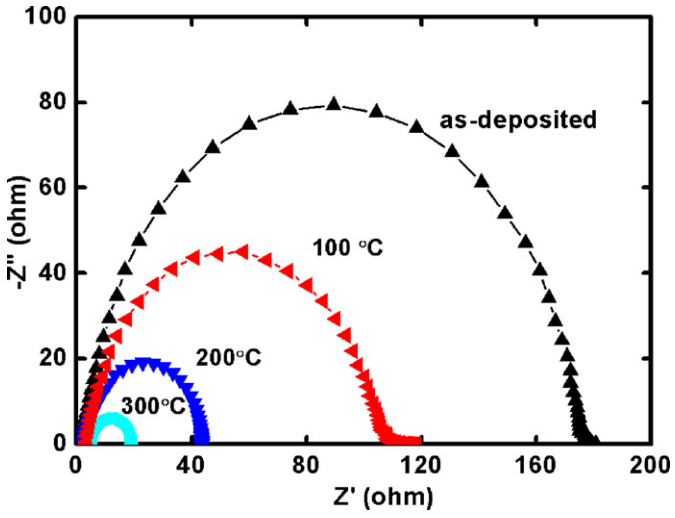

Fig. 4. The complex impedance spectra of LLTO thin films annealed at various temperatures.

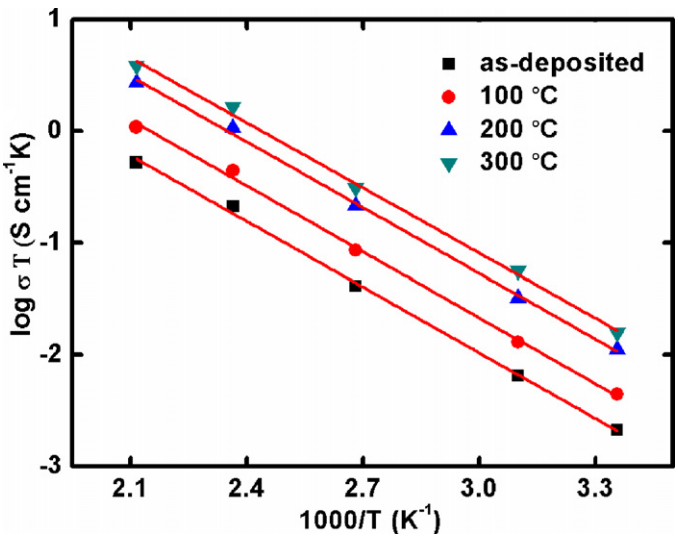

Fig. 5. Arrhenius plots of the conductivity as a function of 1000/T for LLTO thin films annealed at various temperatures.

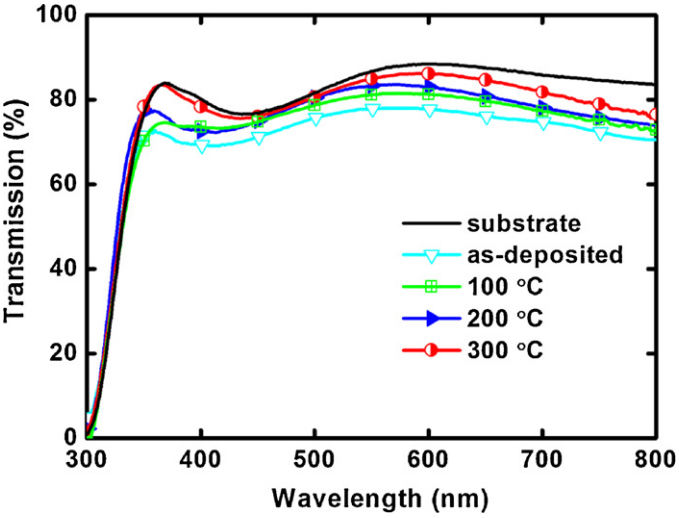

Fig. 6. The UV–Vis transmittance spectra of ITO/glass substrate and LLTO thin films annealed at various temperatures.

where σ_0 is the pre-exponential factor, Ea the activation energy of conduction, T the absolute temperature and k the Boltzman constant. Through the well fitted line of temperature dependence of the ionic conductivity shown in Fig. 5, the activation energy and pre-exponential factor was calculated and summarized in Table 1. Ea values of as-prepared and annealed films are identical to be 0.35 eV. However, the values of pre-exponential factor increase with the elevation of annealing temperature up to 300 °C, which can be interpreted as follows. According to the Nernst–Einstein relationship, the ionic conductivity can be given by,

$$\sigma = \frac{N(Ze)^2 d^2}{kT} \nu_0 \exp\left(\frac{-\mathrm{Ea}}{kT}\right) f \quad (3)$$

where N is the number density of mobile ions, Ze the charge of a mobile ion (in the case of the LLTO, as the mobile ion is Li^+, then $Z = 1$), d the hopping distance of the ion, ν_0 the attempt frequency and f the correlation factor which value would be about 1. Comparing Eqs. (2) and (3), we can see that the pre-exponential factor is connected with the number density, hopping distance and attempt frequency of mobile ions [20], which will be influenced by the annealing process. Therefore, considering the invariance of N and ν_0 in the present situation, the increase of pre-exponential factor should be ascribed to the increase of the hopping distance d with the rise of annealing temperature, which is consistent with the facts of denser, more uniform films obtained through further annealing revealed by 3.1. Certainly, further study should be taken to reveal its real origin.

3.3. Optical properties and film composition

The dependence of optical transmittance on annealing temperature is shown in Fig. 6. The transmittance of all samples is higher than 75%, which can fulfill the transmitting requirement of electrolyte layer in electrochromic devices [4]. With the increase of annealing temperature, the transmittance level in visible spectrum was improved. The transmittance of 300 °C-annealed film was similar to that of substrate, about 85%, which may be attributed to the less light scattering loss due to its smoother, denser and more uniform surface [21].

Based on the above-mentioned analysis, it is easy to draw the conclusion that the optimum processing parameters of LLTO thin films is annealing at 300 °C for 2 h. Therefore the Li/La composition of 300 °C-annealed film was taken by ICP measurement. The results show that the composition of 300 °C-annealed film was $La_{0.41}Li_{0.31}TiO_3$, which does not exactly agree with the target. Surely, this is a typical phenomenon of the sputtering process [19], which is originated form the different sputtering yield for La and Li under the same sputtering conditions.

4. Conclusions

Using RF magnetron sputtering method, LLTO thin films were prepared on ITO/glass substrates from a $La_{0.56}Li_{0.33}TiO_3$ target. The effects of annealing temperature on morphology, structure and photoelectrical properties of prepared films were investigated. The as-deposited and annealed films are amorphous and the surface roughness decreases with the enhancement of annealing temperature up to 300 °C except for the ones annealed at 400 °C. With the increase of annealing temperature (<400 °C), the optical transmittance of LLTO films is enhanced and the ionic conductivity is improved due to a rise of pre-exponential factor in the Arrhenius equation. The highest transmission in visible range and ionic conductivity at room temperature was found for the 300 °C-annealed film ($La_{0.41}Li_{0.31}TiO_3$), namely 85% and 5.25×10^{-5} S cm^{-1}. The LLTO films deposited by RF magnetron sputtering and annealed at 300 °C for 2 h are suitable for application as an electrolyte of all-solid-state electrochromic devices.

Acknowledgements

The authors acknowledge financial support by National Basic Research Program of China (2009CB939704). Natural Science Foundation of China (no. 51032005, 60808024) and the Fundamental Research Funds for the Central Universities (Wuhan University of Technology) and Prof. Moo-Chin Wang (Kaohsiung Medical University) and Dr. Hong-Hsin Huang (Cheng Shiu University) for helpful discussion during the manuscript preparation.

References

[1] J.W. Fergus, J. Power Sources 195 (2010) 4554.
[2] P. Knauth, Solid State Ionics 180 (2009) 911.
[3] C. Bohnke, B. Regray, F.L. Berre, J.L. Fourquet, N. Randrianantoandro, Solid State Ionics 176 (2005) 73.
[4] C.G. Granqvist, Handbook of Inorganic Electrochromic Materials, Elsevier, Amsterdam, 1995.
[5] Y. Inaguma, L. Chen, M. Itoh, T. Nakamura, Solid State Ionics 70–71 (1994) 196.
[6] Y. Inaguma, L. Chen, M. Itoh, T. Nakamura, T. Uchida, H. Ikuta, M. Wakihara, Solid State Commun. 86 (1993) 689.
[7] O. Bohnke, C. Bohnke, J.L. Fourquet, Solid State Ionics 91 (1996) 21.
[8] T. Šalkas, O. Bohnke, J. Macutkevic, A.F. Orliukas, S. Greičius, A. Kezionis, A. Krotkus, R. Sazanouičiené, R. Adomavičius, Phys. Status Solidi (C) 6 (2009) 2756.
[9] H.X. Geng, A. Mei, C. Dong, Y.H. Lin, C.W. Nan, J. Alloys Compd. 481 (2009) 555.
[10] Y. Deng, S.J. Shang, A. Mei, Y.H. Lin, L.Y. Lin, C.W. Nan, J. Alloys Compd. 472 (2009) 456.
[11] A. Mei, X.L. Wang, J.L. Lan, Y.C. Feng, H.X. Geng, Y.H. Lin, C.W. Nan, Electrochim. Acta 55 (2010) 2958.
[12] K. Tajima, Y. Yamada, S. Bao, M. Okada, Y. Yoshimura, J. Phys.: Conf. Ser. 100 (2008) 082017.
[13] K. Tajima, Y. Yamada, S. Bao, M. Okada, K. Yoshimura, J. Electrochem. Soc. 157 (2010) J92.
[14] Y. Yamada, K. Tabata, T. Yashima, Sol. Energy Mater. Sol. Cells 91 (2007) 29.
[15] J.S. Lee, S.J. Chang, J.F. Chen, S.C. Sun, C.H. Liu, U.H. Liaw, Mater. Chem. Phys. 77 (2002) 242.
[16] L.J. Meng, F. Placido, Surf. Coat. Technol. 166 (2003) 44.
[17] S. Stramare, V. Thangadurai, W. Weppner, Chem. Mater. 15 (2003) 3974.
[18] J.K. Ahn, S.G. Yoon, Electrochim. Acta 50 (2004) 371.
[19] J.M. Lee, S.H. Kim, Y. Tak, Y.S. Yoon, J. Power Sources 163 (2006) 173.
[20] S. Furusawa, H. Tabuchi, T. Sugiyama, S. Tao, J.T.S. Irvine, Solid State Ionics 176 (2005) 553.
[21] J.G. Yu, X.J. Zhao, Q.N. Zhao, G. Wang, Mater. Chem. Phys. 68 (2001) 253.