第15卷 第2,3期
2005年9月

广东有色金属学报
JOURNAL OF GUANGDONG NON-FERROUS METALS

Vol. 15, No. 2,3
Sep 2005

Article ID: 1003－7837(2005)02,03－0439－05

Influence of deposition temperature on ionic conductivity of perovskite $(Li_{0.5}La_{0.5})TiO_3$ solid state electrolyte thin film*

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Abstract: Thin film microbattery is a promising micropower source for its high energy density and good cell performances, and the application of fast lithium ion conducting solids as electrolytes is thus very important. $(Li_{0.5}La_{0.5})TiO_3$ (LLTO) thin film electrolytes for thin film microbattery were prepared onto Pt/Si substrates using magnetron sputtering. As-deposited LLTO thin films showed amorphous-like phases and when deposition temperature increases the ionic conductivity raises accordingly. The ionic conductivity of LLTO thin film reaches 8.7×10^{-6} S/cm when the deposition temperature is 400℃, which shows that the LLTO thin films deposited by magnetron sputtering are suitable for application as an electrolyte for thin film microbattery.

Key words: $(Li, La)TiO_3$; solid state electrolyte; magnetron sputtering; thin film microbattery; ionic conductivity

CLC number: TM911.1 **Document code**: A

1 Introduction

With the development of electronic devices, thin film microbatteries have received great attention because they can be completely integrated with microcircuits, such as microdevices, microsensors, and very-large-scale integration (VLSI)[1-3]. The thin film microbattery is a promising alternative micropower source because of its high energy density and good cell performances, which was fabricated by depositing thin films of the cell components, i. e. cathode, electrolyte, anode, and current collectors. The amorphous glassy thin film electrolyte, which plays as fast lithium ion conductor, is a key factor in the application of thin film microbattery. An ideal solid electrolyte requires high ionic conductivity, low electronic conductivity, good thermal stability, and resistance to dielectronic breakdown at the voltage at which the batteries operate. J. B. Bates, *et al.*[4] have done much work in preparing lithium silicophosphate (LIPON) thin film electrolytes. The thin films were deposited by RF magnetron sputtering from a Li_3PO_4 target in nitrogen

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Received date: 2005－06－29

* **Foundation item**: Innovation Fund(No. 82236) of General Research Institute for Nonferrous Metals (GRINM)

Biography: SHEN Wan(born in 1980), Male, Master reactive plasma and the ionic conductivity of LiPON thin film electrolyte is 2×10^{-6} S/cm at room temperature. LIPON electrolyte thin films have relatively high ionic conductivity at room temperature and showed stable cycleability of more than 3000 cycles, but their disadvantage easy to react with oxygen and moisture in the air is obvious and thus limited their application.

The high ionic conductivity in lithium lanthanum titanate(LLTO) was firstly reported by A. G. Belous, *et al.*[5] in 1987, and Inaguma, *et al.* investigated it further after that and reported perovskite $(Li_{0.5}La_{0.5})TiO_3$ in bulk exhibited lithium ion conductivity as high as 1×10^{-3} S/cm at room temperature[6]. Such a high conductivity is considered to come from the presence of a vacancy on the A-site and a lot of equivalent sites for the lithium ion to occupy and freely move in the A-site space of perovskites. Concerning the preparing methods of LLTO thin film, there are some reports[7] mentioned pulsed laser deposition but no report on magnetron sputtering to the authors' best knowledge. From such background we have been studying the preparation and the properties of the LLTO thin films. In this study, LLTO thin films with an amorphous phase was prepared onto Pt collector using magnetron sputtering at different deposition temperatures and electrical properties of thin films were investigated.

2 Experimental

LLTO thin films was prepared onto Pt/ Si substrate using R. F. magnetron sputtering at different deposition temperatures of 200℃, 250℃, 300℃, 350℃, 400℃ and the corresponding thin film samples were numbered A, B, C, D and E, respectively. For AC impedance measurements of LLTO thin film, a layer of Pt was deposited on the silicon substrate beforehand and then a LLTO thin film and a layer of Pt respectively, in order to form a Pt | LLTO | Pt sandwich structure. The Si(100) substrate(10 mm×10 mm) used as film support was cleaned by $H_2SO_4+K_2CrO_4$ solution, cleaned in ethanol ultrasonically, and then blown dry in nitrogen gas. Thin films were deposited in Ar atmosphere with a target-to-substrate distance of 70 mm. The Si(100) substrates were rotated for homogeneous deposition during the sputtering process. A molecule pump with a coupled rotary pump was used to achieve an ultimate pressure of 8×10^{-5} Pa before introducing Ar, and a flow controller was used to monitor the gas flow. The work pressure was kept to 1.0 Pa. High purity Li_2CO_3, La_2CO_3 and TiO_2 mechanically mixed at 1 : 1 : 4 mole ratio were used as starting materials for LLTO targets. The powders were calcined at 1200℃ for 6 h in air and the calcined powder was ground with ethanol, pressed into a disk with a diameter of 60mm and a thickness about 10mm by cold isostatic pressing (CIP). The formed target was sintered at 1300℃ for 5 h with a heating rate of 2℃/min in air and cooled to room temperature. Then the sintered target was weared away to a diameter of 51 mm and a thickness about 3mm in order to be installed in the magnetron sputtering system.

X-ray diffraction (XRD, Rigaku, Japan) using Cu Kα radiation was carried out to determine the crystal structure of the films. X-ray photoelectron spectra (XPS, MKII, VG) was used to determine surface chemical composition of the thin films with a Mg anode X-ray source operating at 300 W. The high-resolution multiplex was taken by using an analyzer with a 35.75 eV pass energy. A profilometry(Sloan dektak II) was used to measure the thickness of the thin film. AC impedance measurements(EG&G M388, Model 273A) to determine ion conductivities were made at frequencies from 1Hz to 1MHz at room temperature.

3 Results and discussion

The X-ray diffraction pattern of prepared LLTO powders is given in Fig. 1. The powder X-ray diffraction pattern indicates that the primitive cell possesses a cubic system with perovskite structure. Broad and weak intensity peaks arising from the superlattice with the double period of c-axis were observed. The superlattice lines were considered to correspond to the ordering of La^{3+} and Li^+ or vacancy. There are considerable large amount of equivalent sites for lithium ion in LLTO. La^{3+} and TiO_6 octahedra construct the rigid structure with statically distributed lithium ions. As-deposited LLTO thin films showed amorphous structure and the X-ray diffraction pattern will not be presented in this article. To solid state electrolyte thin film, the structure of amorphous film has more vacancies for lithium ion moving and conducting, and thus decreased its activation energy. Therefore, the ionic conductivity of amorphous electrolyte thin film is much higher than that of the crystalline state electrolyte.

XPS spectrum of LLTO thin film is presented in Fig. 2. The chemical composition of electrolyte thin film is determined using $Cx=(I_1/\alpha_1)/(\sum I_n/\alpha_n)$, where Cx is sample's atomic percentage concentration, I the elementary intensity and α_n the sensitivity factor. The spectrum of La 3d 5/2, as shown in Fig. 2, can be fitted with two peaks separated by about 4. 3 eV. Different opinions are found in the literature about the fine structure observed around the La 3d line. Wang *et al.* attributed it to inequivalent La atoms for the $La_{1-x}Sr_xCoO_{3-d}$ compound[8]. However, it was also considered to be caused by the interatomic electron transfer from ligand to metal 3d orbitals. There is a general agreement in the literature on XPS, that the double peak structure of each spin-orbital component of La 3d reflects states with the configuration $3d^9 4f^0 L$ and $3d^9 4f^1 L$ where L denotes the oxygen ligand and underscoring denotes a hole[9]. Recently, Teterin *et al.* proposed it is due to the secondary electronic processes accompanying the photoemission, such as shake-up/down processes and dynamics effect[10].

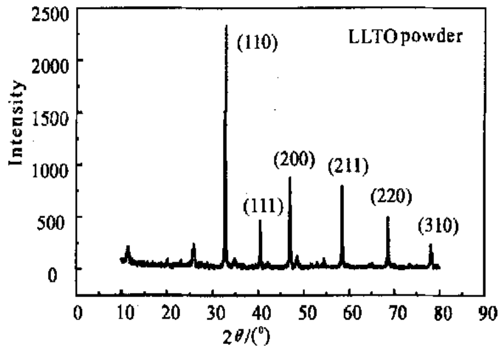

Fig. 1 XRD patterns of LLTO powder

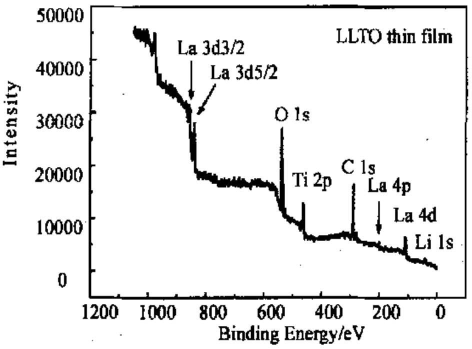

Fig. 2 Integral XPS spectrum of LLTO thin film

Sample AC impedance spectras of the sandwich structured LLTO electrolyte thin film measured at room temperature are shown in Fig. 3. The impedance spectrum consists of a high frequency semi-circle and a low frequency inclined line. The high frequency semi-circle can be regarded due to the bulk LLTO thin film, and the inclined line comes from the blocking electrode system of the Pt | electrolyte | Pt sandwich structure, and the gradient is ascribed to the interfacial roughness between electrolyte thin film and Pt electrodes. The influence of grain boundaries on the conductivity was not observed from Fig. 3 and it may come from the thin film of amorphous structure. The ionic conductivity was determined from R by selecting the Z_{Re} value at the frequency at which Z_{Im} goes through a local minimum and can be calculated from $\sigma=(d/A)/R$, where d is the film thickness, A is the area of the metal contact, and R is the film resistance. The relationship between the deposition temperature and Z_{Re} value is given in Fig. 4. It shows that the Z_{Re} value increases when the deposition temperature increases correspondingly. When the thickness and area of the metal contact of the thin films are determinate, a higher Z_{Re} value is beneficial to improve ionic conductivity. Fig. 5 presents the relationship between deposition temperature and ionic conductivity of the films.

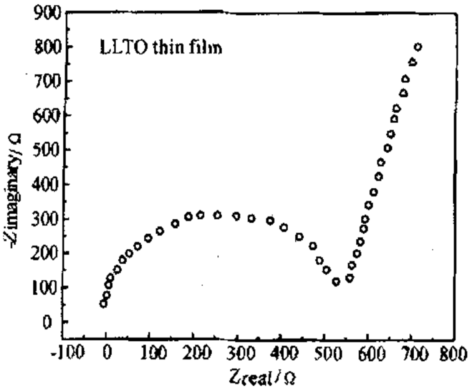

Fig. 3 Nyquist AC impedance spectra of LLTO thin film

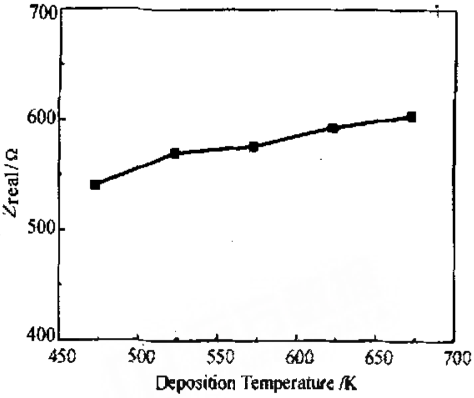

Fig. 4 Relationship between the deposition temperature and Z_{Re} value

When deposition temperature increases the ionic conductivity raises accordingly. While the deposition temperature is 400℃, the ionic conductivity reaches 8.7×10^{-6} S/cm. This shows that the LLTO thin films deposited by magnetron sputtering are suitable for application as an electrolyte for thin film microbattery.

4 Conclusion

$(Li_{0.5}La_{0.5})TiO_3$ (LLTO) thin film electrolytes for thin film microbattery were prepared onto Pt/Si substrates using magnetron sputtering. LLTO thin film as-deposited showed an amorphous-like phase. The ionic conductivity of as-deposited LLTO thin film is 8.7×10^{-6} S/cm measured at room temperature when the deposition temperature is 400℃, which showed that the LLTO thin films deposited by magnetron sputtering are suitable for application as an electrolyte for thin film microbattery.

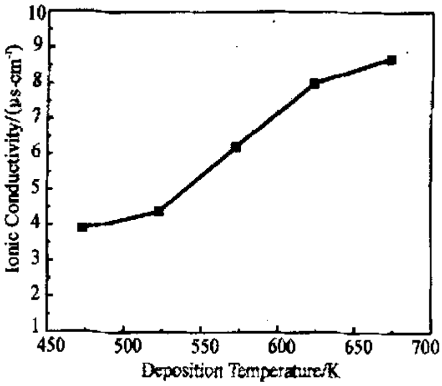

Fig. 5 Relationship between deposition temperature and ionic conductivity

Acknowledgements

This work was supported by the Innovation Fund(No. 82236) of General Research Institute for Nonferrous Metals (GRINM) and their support is gratefully acknowledged.

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