

Short communication

Solid-state thin-film supercapacitor with ruthenium oxide and solid electrolyte thin films

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Abstract

Direct current reactive sputtering deposition of ruthenium oxide thin films (bottom and top electrodes) at 400°C are performed to produce a solid-state thin-film supercapacitor (TFSC). The supercapacitor has a cell structure of RuO₂/Li_{2.94}PO_{2.37}N_{0.75} (Lipon)/RuO₂/Pt. Radio frequency, reactive sputtering deposition of an Li_{2.94}PO_{2.37}N_{0.75} electrolyte film is performed on the bottom RuO₂ film at room temperature to separate the bottom and top RuO₂ electrodes electrically. The stoichiometry of the RuO₂ thin film is investigated by Rutherford back-scattering spectrometry (RBS). X-ray diffraction (XRD) shows that the as-deposited RuO₂ thin film is an amorphous phase. Scanning electron microscopy (SEM) measurements reveal that the RuO₂/Lipon/RuO₂ hetero-interfaces have no inter-diffusion problems. Charge–discharge measurements with constant current at room temperature clearly reveal typical supercapacitor behaviour for a RuO₂/Lipon/RuO₂/Pt cell structure. Since the electrolyte thin film has low ionic mobility, the capacity and cycle performance are inferior to those of a bulk type of supercapacitor. These results indicate that a high performance, TFSC can be fabricated by a solid electrolyte thin film with high ionic conductivity. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

In recent years, micro-electronic system technologies have attracted attention world-wide for many applications which include medical and communication equipments, sensors and actuators [1–4]. The benefits offered by such technologies are low cost, small size, high reliability and low weight. There are, however, many technical problems with the development of these types of micro-devices. One of the most important challenges is to develop the optimal micro-power source to drive these devices. The thin film battery (TFB) has attracted special attention [5–10]. Even though the TFB has high specific energy and high specific power, it may have insufficient power to drive micro-electronic devices with digital mode because peak input power may be required in a very short time. A supercapacitor can meet this specification since it has a much higher specific power than the TFB and can supply this power rapidly. Many studies of bulk-type supercapacitors have been reported [11,12]. To the best of our knowledge, however, no research

groups have studied a thin-film supercapacitor (TFSC) with a solid electrolyte thin film.

This communication reports the fabrication process and electrochemical properties of a solid-state TFSC with a RuO₂/Li_{2.94}PO_{2.37}N_{0.75} (Lipon)/RuO₂/Pt structure. Since studies by Bates et al. [13] and Jeon et al. [14] have demonstrated that the Lipon thin-film electrolyte is suitable for a TFB, it would appear reasonable that this material is also suitable for investigating the possibility of a TFSC.

2. Experimental

The (1 0 0) silicon substrates were degreased in acetone, methanol and ethanol for 5 min, and then rinsed thoroughly in deionized water. Next, a TiO₂ (300 Å) glue layer and a Pt (2000 Å) current-collector layer were deposited by a radio-frequency (r.f.) method and a direct current (dc) in situ sputtering method, respectively. After preparation of the substrate, a vacuum chamber was evacuated to 1×10^{-5} Torr and the bottom RuO₂ thin-film electrode was deposited by means of an on-axis dc reactive sputtering method which used 2 in. ruthenium metal target with a

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purity of 99.95%, a working pressure of 10 mTorr, and a dc power of 200 W. The gas flow ratio of oxygen to argon was 0.3. The deposition temperature and time were 400°C and 20 min, respectively.

The Lipon electrolyte film was deposited ex situ on to the as-deposited RuO₂ thin film with a different on-axis r.f. reactive sputtering system at room temperature. The deposition process and characteristics of the Lipon thin film have been discussed in our previous report [10]. The same procedure was used to fabricate the top RuO₂ thin film electrode as for the bottom RuO₂ electrode. Rutherford back-scattering spectroscopy (RBS) and X-ray diffraction (XRD) measurements were conducted to investigate, respectively, the stoichiometry and the crystallinity of the as-deposited thin films of RuO₂. Scanning electron microscopy (SEM) observations were performed to examine the surface and the cross-sectional structures of the films. Charge-discharge measurements at room temperature were carried out to measure the supercapacitor properties of the RuO₂/Lipon/RuO₂ TFSC structure. The constant current density and the cut-off voltage range were 100 $\mu\text{A cm}^{-2}$ and 0–2.5 V, respectively. The major fabrication steps employed to produce the TFSC with a RuO₂/Lipon/RuO₂/Pt/TiO₂/Si structure are shown in Fig. 1.

3. Results and discussion

The as-deposited ruthenium oxide films had mirror-like surfaces without any indication of defects such as cracks, pores, pinholes and/or voids. The defect-free nature was deduced from observations with the naked eye and with Normarski optical microscopy. Alpha-step measurements showed a typical film thickness of about 0.2 μm or a growth rate of 100 \AA min^{-1} . The RBS yield-channel plot for the as-deposited ruthenium oxide film is presented in Fig. 2. The

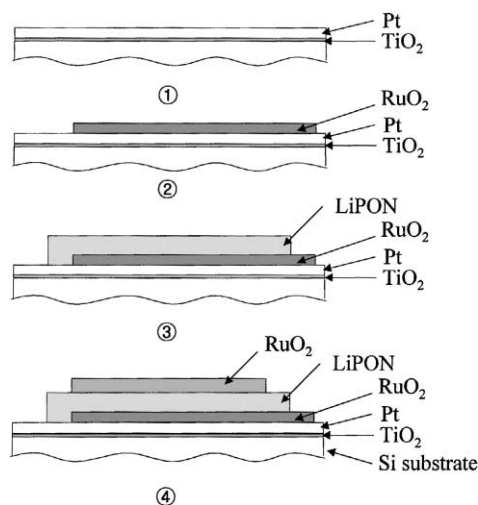


Fig. 1. Major fabrication steps for a TFSC with a RuO₂/Lipon/RuO₂/Pt/TiO₂/Si structure.

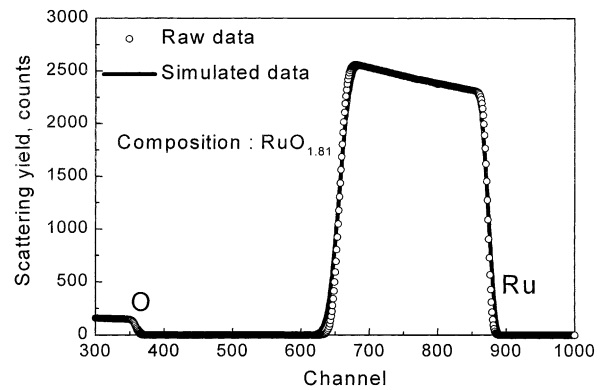


Fig. 2. RBS yield-channel plot for as-deposited ruthenium oxide film.

RBS simulation confirmed that the ratio of O to Ru was around 2.05. This result suggests that the as-deposited film is the RuO₂ phase. According to the RBS simulation, the RuO₂ thickness is 2000 \AA , a finding which is in good agreement with the Alpha-step result.

Since amorphous RuO₂ has a much higher capacity (350 F g^{-1}) than crystalline RuO₂ in a bulk-type supercapacitor [15,16], it is desirable to deposit an amorphous RuO₂ film. The XRD pattern is shown in Fig. 3. No crystalline peaks of the RuO₂ film were shown, that is, the as-deposited RuO₂ film was an amorphous phase.

Scanning electron microscopy of the surface of the as-deposited RuO₂ film on the Pt current-collector and of the cross-section of RuO₂/Lipon/RuO₂ TFSC structure are shown in Fig. 4. The surface of the RuO₂ thin film consists of small size grains. There are no defects such as cracks, voids or impurity particles. The interface also does not show any indication of defects. Since interface defects can act as traps for the ions in electrolyte, the sharp interface structure is very desirable for the fabrication of a high-performance TFSC.

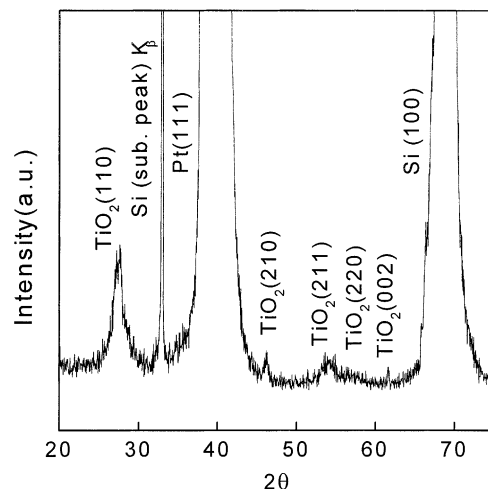


Fig. 3. XRD spectrum for as-deposited RuO₂ film on Pt/TiO₂/Si substrate.

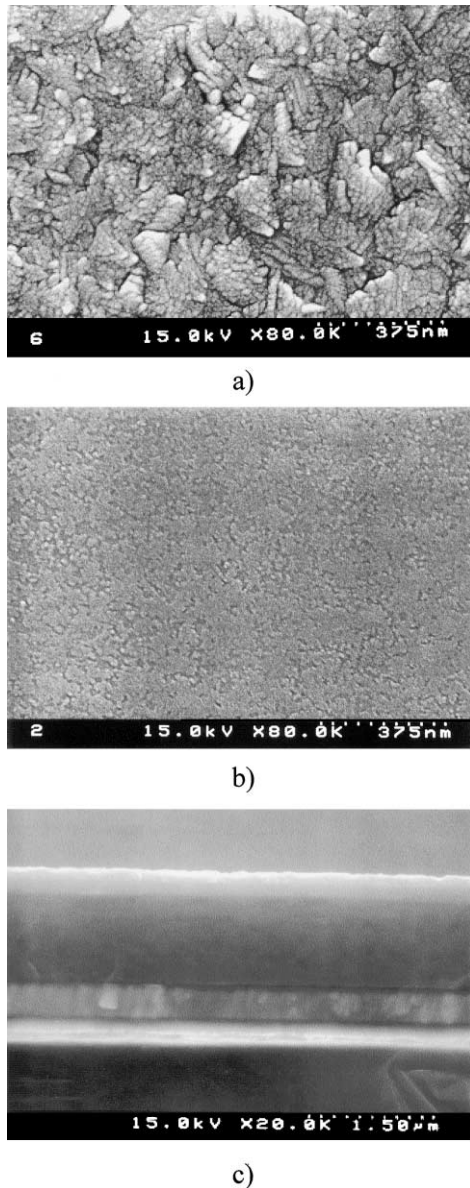


Fig. 4. Scanning electron microscopy of (a) as-deposited RuO₂ film; (b) Lipon on RuO₂ film; (c) cross-section of RuO₂/Lipon/RuO₂ TFSC.

The charge–discharge and the capacity–cycle behaviour of the as-fabricated RuO₂/Lipon/RuO₂/Pt TFSC structure at room temperature is given in Fig. 5. These are very similar to those of a bulk-type supercapacitor. The capacity can be calculated from the time–voltage curves. In contrast with liquid electrolyte, however, the charge–discharge and the capacity–cycle curves show a relatively larger current–resistance (IR) drop and a faster capacity decrease than for the bulk-type supercapacitor. In the RuO₂/Lipon/RuO₂/Pt TFSC structure, the effective reaction of the TFSC can be presented by $\text{RuO}_2 + x\text{Li}^+$ (from the Lipon) + $x\text{e}^- \leftrightarrow \text{Li}_x\text{RuO}_2$. Some of the Li⁺ ions might not be de-intercalated from the RuO₂ electrode during the discharge process because of the fast electron current sweep, which forms an ionic repulsion against the charged Li⁺ ions during the charge process. That

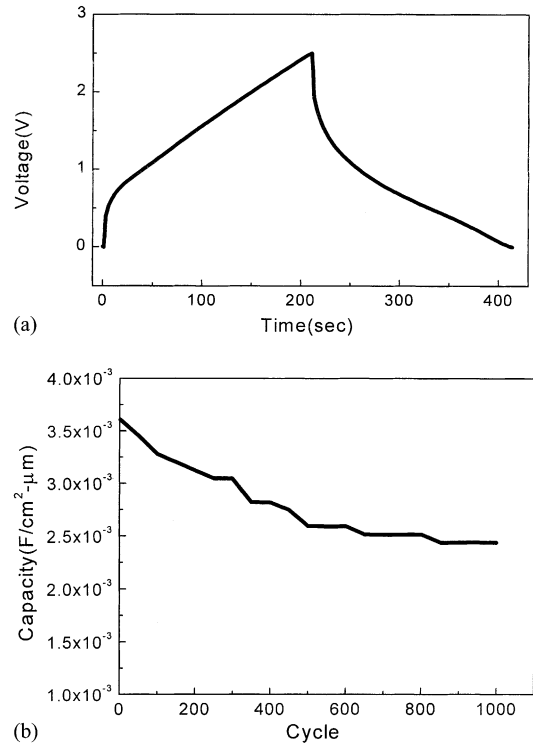


Fig. 5. (a) Charge–discharge and (b) capacity–cycle behaviour of TFSC with RuO₂/Lipon/RuO₂ structure.

is, the IR drop and the capacity degradation might originate from the lower ion mobility of Li⁺ ions in the Lipon electrolyte than that of H⁺ and OH[−] ions in the liquid electrolyte. This suggests that solid-electrolyte thin films with high ionic conductivity such as Ta₂O₅ with H⁺ hold promise for a TFSC with high capacity and high cycle life.

4. Conclusions

Charge–discharge measurements with constant current density at room temperature show that a TFSC with a RuO₂/Lipon/RuO₂/Pt/TiO₂/Si structure has typical supercapacitor behaviour, although it has a larger IR drop and a faster capacity decrease than a bulk-type supercapacitor with liquid electrolyte. These findings suggest that a high-performance TFSC can be made with a solid electrolyte thin film with high ionic mobility. With careful choice of a solid electrolyte that has a small radius of mobile ion or fast ion mobility, it should be possible to produce a high performance TFSC. Furthermore, by virtue of its high specific power the TFSC shows promise for a hybrid system with a thin-film battery that can be used in the fabrication of on-chip electronic devices.

References

- [1] Y.S. Yoon, J.H. Kim, A.M. Schmidt, D.L. Polla, Q. Wang, W.L. Gladfelter, Y.H. Shin, *J. Mater. Sci. (Mater. Electr.)* 9 (1999) 465.

- [2] Y.S. Yoon, J.H. Kim, D.L. Polla, Y.H. Shin, *Jpn. J. Appl. Phys.* 37 (1998) 7129.
- [3] K. Kanehori, K. Matsumoto, K. Miyauchi, T. Kudo, *Solid State Ionics* 9/10 (1983) 1445.
- [4] A. Levasseur, M. Kbala, P. Hagenmuller, G. Couturier, Y. Danto, *Solid State Ionics* 9/10 (1983) 1439.
- [5] J.H. Kennedy, *Thin Solid Films* 43 (1977) 41.
- [6] S. Sekido, *Solid State Ionics* 9/10 (1983) 777.
- [7] A. Levasseur, M. Menetrier, R. Dormoy, G. Meunier, *Mater. Sci. Eng. B3* (1989) 5.
- [8] M.S. Whittingham, *J. Electrochem. Soc.* 123 (1976) 315.
- [9] A.J. Jacobson, R.R. Chianelli, S.M. Rich, M.S. Whittingham, *Mater. Res. Bull.* 14 (1979) 1437.
- [10] E.J. Jeon, Y.H. Shin, S.C. Nam, W.I. Cho, Y.S. Yoon, *J. Korean Inst. Electric. Electron. Mater. Eng.* 12 (1999) 1019.
- [11] L. Bonnefoi, P. Simon, J.F. Fauvarque, C. Sarrazin, J.F. Sarrau, A. Dugast, *J. Power Sources* 80 (1999) 149.
- [12] I. Bispo-Fonseca, J. Aggar, C. Sarrazin, P. Simon, J.F. Fauvarque, *J. Power Sources* 79 (1999) 238.
- [13] J. Bates, N.J. Dudney, G.R. Gruzalski, R.A. Zuhr, A. Choudhury, C.F. Luck, J.D. Robertson, *Solid State Ionics* 53 (1992) 647.
- [14] E.J. Jeon, Y.S. Yoon, S.C. Nam, W.I. Cho, Y.W. Shin, *J. Korean Electrochem. Soc.* 3 (2000) 115.
- [15] J.P. Zheng, P.J. Cygan, T.R. Jow, *J. Electrochem. Soc.* 142 (1995) 2699.
- [16] J.P. Zheng, T.R. Jow, Q.X. Jia, X.D. Wu, *J. Electrochem. Soc.* 143 (1996) 1068.