

ICAPMA_2017

Lithium storage performance of copper nitride films deposited by reactive DC magnetron sputtering

Suchat Suwannatus^{a,*}, Boonchai Duangsawat^b, Udomdej Pakdee^c

^a Department of Physics, Faculty of Science, Kasetsart University, Bangkok 10900, Thailand,

^b Division of Chemistry, Department of Science, Faculty of Science and Technology, Rajamangala University of Technology Krungthep, Bangkok 10120, Thailand,

^c Division of Physics, Department of Science, Faculty of Science and Technology, Rajamangala University of Technology Krungthep, Bangkok 10120, Thailand

Abstract

Copper nitride (Cu_3N) films were deposited on copper foil substrates by reactive direct current (DC) unbalance magnetron sputtering. The Cu_3N films with DC sputtering powers of 110, 205, 280 and 373 W under the mixture of argon (Ar) and nitrogen (N_2) gases were investigated. The dependence of crystalline structure and film thickness of Cu_3N on the sputtering powers was evaluated. Exclusively, the electrochemical measurements of the films in 1M LiCl as electrolyte were also carried out. The good performance of lithium ion storage was observed. These results demonstrate that Cu_3N film on copper foil could be further explored as high capacity material for flexible lithium ion battery development.

© 2018 Elsevier Ltd. All rights reserved.

Selection and/or Peer-review under responsibility of 3rd International Conference on Applied Physics and Materials Applications.

Keywords: Copper nitride film; Magnetron sputtering; Lithium ion storage

1. Introduction

Transition metal nitride films have been focused on the various applications due to their outstanding properties such as, optical, electrical and energy storage properties [1-8]. Most of these applications have been concentrated on the lithium ion (Li-ion) batteries [9]. Copper nitride (Cu_3N) film has been focused as a candidate in electrochemical applications due to their low cost, long lifetime and high stability [10-11]. This semiconducting film is a good

* Corresponding author. Tel.: +66-02-562-5555; fax: +66-02-942-8029.

E-mail address: fsciscs@ku.ac.th

medium for various mass storages including a charge storage application [12]. In the growth technique, the heated substrate was employed to achieve better crystallinity of the films [13]. However, the simple decomposition of Cu_3N into Cu and N_2 at low temperature (300–400 °C) is the obstruction for the growth of a good crystalline quality [14]. Therefore, the high crystalline growth of Cu_3N films at room temperature is challenging. In a literature, Cu_3N film was prepared as composites using acetylene black and a polyvinylidene fluoride (PVDF) binder in from of an ink onto a copper foil. This film was used as negative electrode materials for sodium batteries [15]. However, the addition of some binders into the electrode material may increase the electrical contract resistance. Hence, the direct growth of effective Cu_3N film on an electrical conductive substrate would provide a good electrical contract. Furthermore, the Cu_3N films deposited on the flexible substrates are well-fitting for flexible battery development.

In this work, the high crystalline Cu_3N films were deposited directly on copper foils as the flexible substrates at room temperature. During the growth of Cu_3N films, the Cu target was supplied at various DC sputtering powers of 110, 205, 280 and 373 W under the combination of argon (Ar) and nitrogen (N_2) gases. The effects of sputtering powers on the growth of Cu_3N films were reported. Furthermore, these films were tested as the electrode in a lithium-ion solution, and an electrochemical performance was also observed.

2. Experimental

The Cu_3N films were deposited by a home-made reactive DC magnetron sputtering. Oxygen free copper foils (~50 μm thick) purchased from Brastech Company were used as the flexible substrates for all Cu_3N film growth conditions. Before the process, the copper foils were ultrasonically cleaned in acetone first followed by methanol for 10 min and dried with nitrogen before loading into the chamber of sputtering system. The chamber was evacuated to obtain a base pressure of 5×10^{-5} mbar using a pumping system composed of a rotary pump and a diffusion pump. Argon was fed into the chamber with a flow rate of 4.5 sccm until the working pressure is raised to 4×10^{-3} mbar. The reactive nitrogen gas was fed into the chamber with a flow rate of 1.5 sccm. During the process, the Cu target was supplied by a DC power source with the deposited time of 5 min. The DC power was kept at 110 W, 205 W, 280 W and 373 W in each condition. After the process, the crystallinity of the Cu_3N films was determined by X-ray diffraction (XRD, Bruker D8 Advance). The thickness of Cu_3N films was studied using scanning electron microscopy (SEM, Quanta 450 FEI). The electrochemical behavior of Cu_3N electrodes was examined using a potentiostat (Autolab PGSTAT-12).

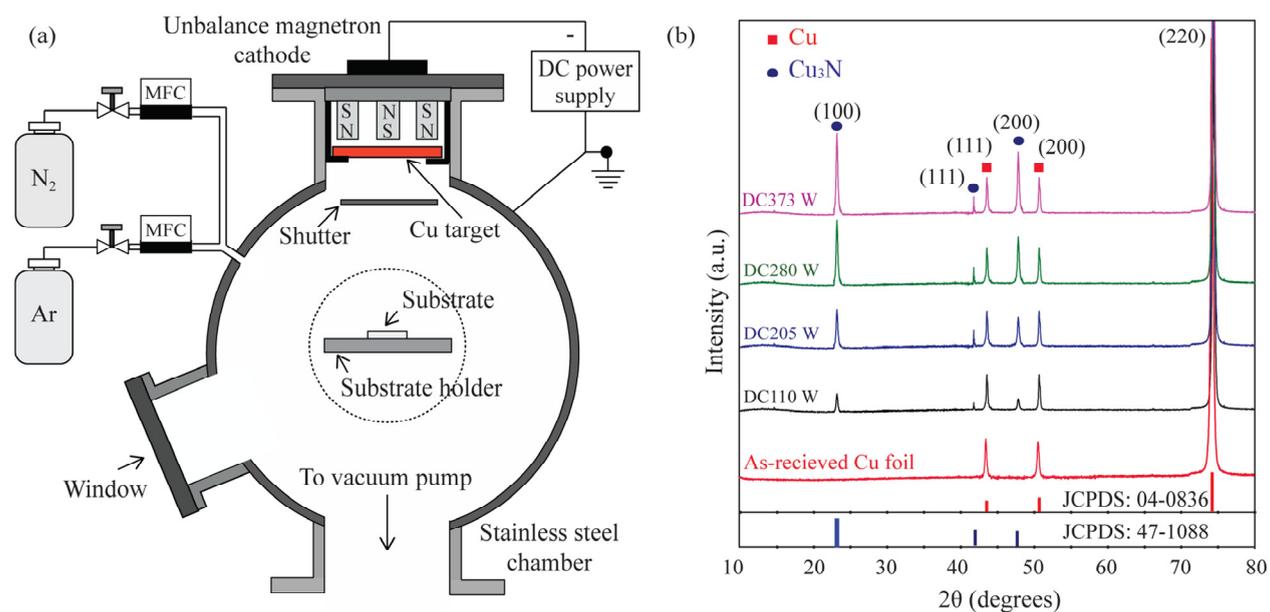


Fig. 1. (a) Schematic image of a home-made sputtering and (b) XRD patterns of Cu_3N films.

3. Results and discussion

The schematic image of a home-made DC sputtering system and XRD patterns are shown in Fig. 1a and Fig. 1b, respectively. The XRD pattern has been widely used to refer the crystallinity of the films. The strong peak is indicative the high crystallinity and the perfection of film structure. The XRD pattern of an as-receive Cu foil is demonstrated as a reference. This pattern clearly demonstrates (111), (200) and (220) peaks of Cu structure according to the JCPDS number of 04-0836. The XRD patterns of coated Cu_3N film on Cu foil without any annealing were observed. The (100), (111) and (200) peaks correspond to the Cu_3N with the JCPDS number of 47-1088. It can be seen that the intensity of the all Cu_3N peaks increased with increasing sputtering power. The intensity of Cu_3N at DC373 W is the strongest. Therefore, the crystallinity of Cu_3N films is a function of sputtering powers.

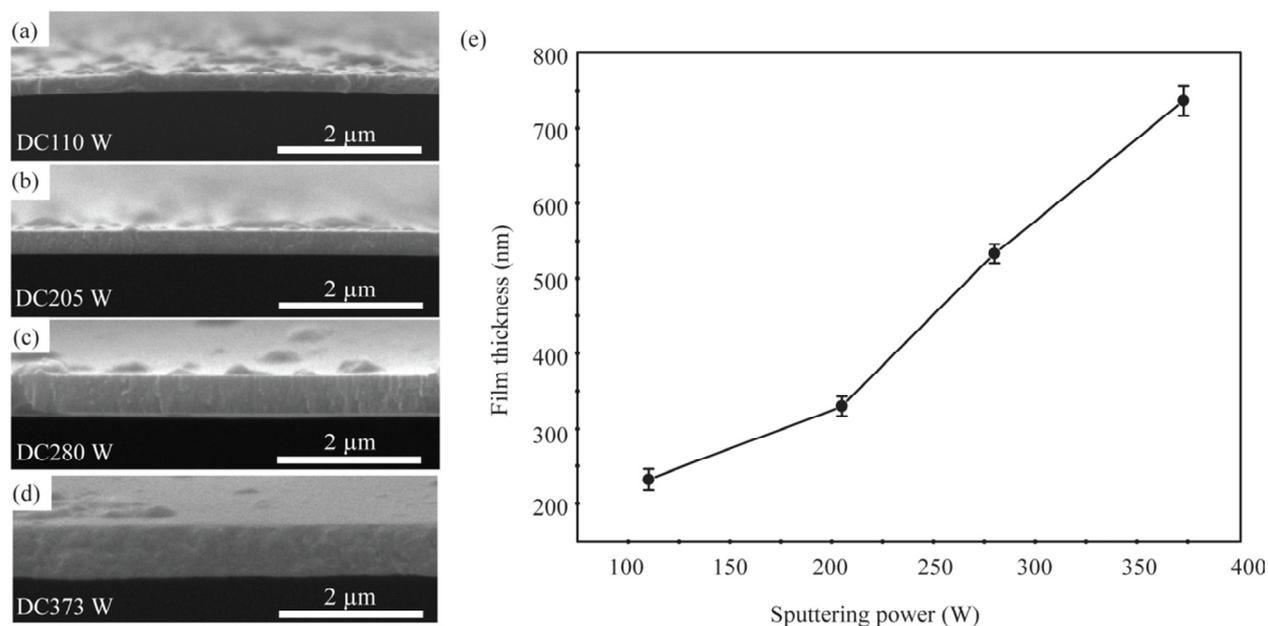


Fig. 2. Left column: Cross-sectional SEM images of Cu_3N films at different DC powers of (a) 110 W, (b) 205 W, (c) 280 W and 373 W. Right column: (e) Dependence of Cu_3N film thickness on different DC sputtering powers. Error bars are based on repeated measurements.

As can be seen in Fig. 2(a)-2(d), the average thicknesses of Cu_3N films deposited with sputtering powers of 110, 205, 280 and 373 W are 232, 330, 533 and 736 nm, respectively. The dependence of Cu_3N film thickness on the different DC sputtering powers is shown in Fig. 2(e). It is clearly seen that the thickness of Cu_3N film increased with increasing sputtering power.

Fig. 3 shows the electrochemical measurements of Cu_3N films deposited on copper foils using 1M LiCl as electrolyte. Before the measurements, the insulating epoxy was coated on the back side of the film substrates for preventing the charge build up effect. The rectangular-like shape of cyclic voltammograms (CV) shown in Fig. 3(a) indicated the capacitor behavior of all Cu_3N films. The largest contour area was observed at DC110W condition. Therefore, the storage capacity is better when the film is thin. It also observes stable impressive performance shown in Fig. 3(b) that the Cu_3N films do not break down even after 50 cycles at a constant scan rate of 100 mV s^{-1} . The charge and discharge curves for different DC sputtering powers of 110, 205, 280 and 373 W are shown in Fig. 3(c). For the discharge curves, the sequential decreasing rates were observed. The slowest rate of Cu_3N film electrode was shown at the low sputtering power of 110 W. It is the ideal property of capacitor. Therefore, these results strongly confirmed that the electrochemical performance of Cu_3N in 1M LiCl electrolyte depended on the DC sputtering powers.

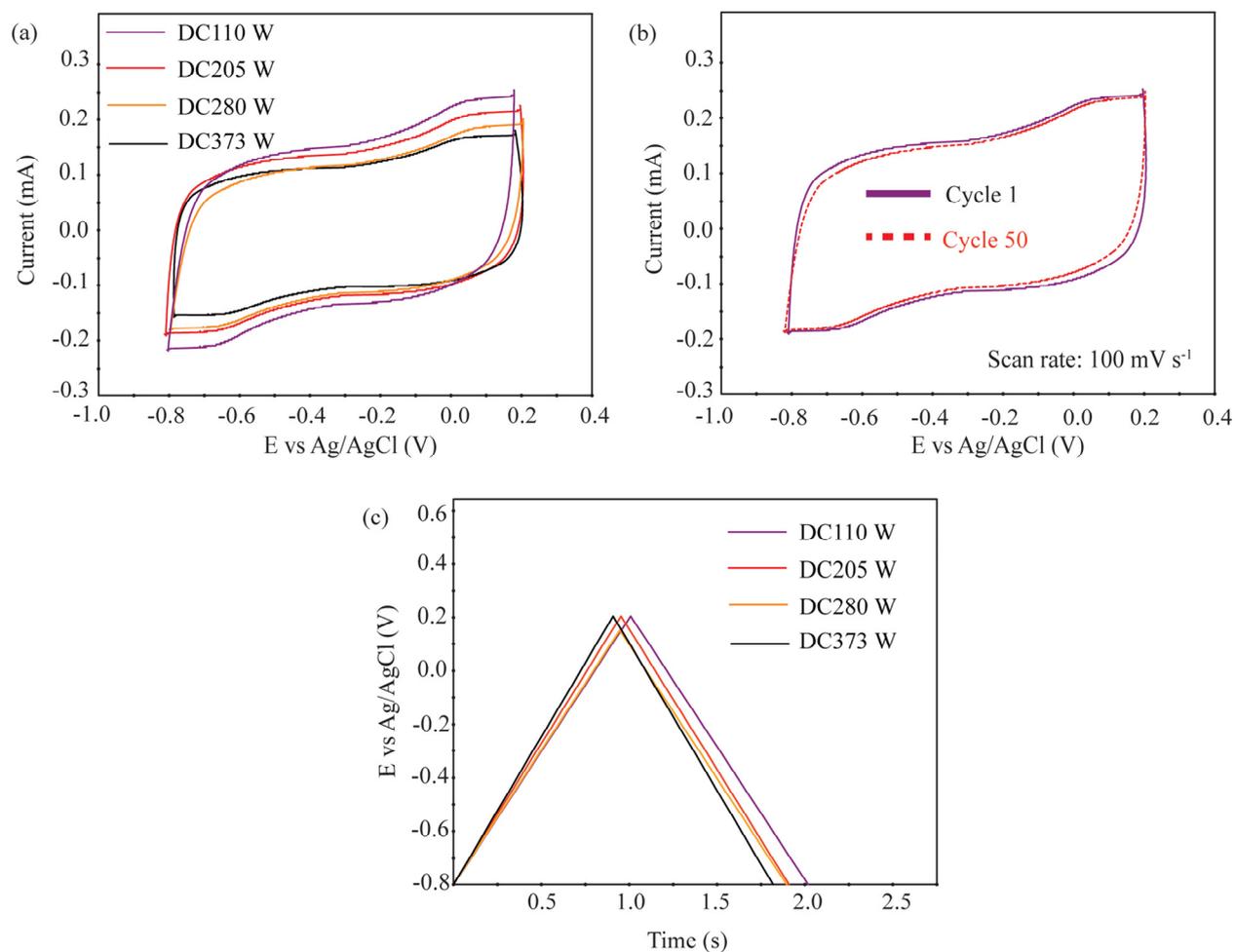


Fig. 3. Electrochemical measurements of Cu_3N deposited on copper foils using an electric potential from -0.8 to 0.2 V: (a) CV measurements for different DC sputtering powers (b) CV measurements at a scan rate of 100 mV s^{-1} for cycle 1 and cycle 50 and (c) Charge and discharge curves for different DC sputtering powers of 110, 205, 280 and 373 W.

4. Conclusions

In this work, Cu_3N films were successfully deposited on copper foils with different copper contents using DC magnetron sputtering. The DC sputtering powers of 110, 205, 280 and 373 W were studied on the film thicknesses, crystallinities and electrochemical behaviors of the Cu_3N films. The XRD patterns and the cross-sectional SEM images indicated that the crystallinities and film thicknesses of Cu_3N depended on the sputtering powers. The electrochemical behaviors of the all films demonstrated the good performance of lithium ion storage. The best performance of the films was observed for the DC110W condition. Therefore, the storage capacity is better when the film is thin. Finally, the Cu_3N films may be the good candidate in combination with other electrode materials as high capacity material for lithium ion batteries.

Acknowledgements

This study is financially supported by Faculty of Science, and in part by Kasetsart University.

References

- [1] Z. Ji, Y. Zhang, Y. Yuan, C. Wang, *Mater. Lett.* 60 (2006) 3758-3760.
- [2] C. Gallardo-Vega, W. de la Cruz, *Appl. Surf. Sci.* 252 (2006) 8001-8004.
- [3] Y. Zhao, J. Zhao, T. Yang, J. Zhang, J. Yang, X. Li, *Ceram. Int.* 42 (2016) 4486-4490.
- [4] I.M. Odeh, *J. Alloys Compd.* 454 (2008) 102-105.
- [5] G.H. Yue, P.X. Yan, J. Wang, *J. Cryst. Growth* 274 (2005) 464-468.
- [6] C.M. Caskey, R.M. Richards, D.S. Ginley, A. Zakutayev, *Mater. Horiz* 1 (2014) 424-430.
- [7] X.M. Yuan, P.X. Yan, J.Z. Liu, *Mater. Lett.* 60 (2006) 1809-1812.
- [8] D.M. Borsa, D.O. Boerma, *Surf. Sci.* 548 (2004) 95-105.
- [9] D. Kundu, F. Krumeich, R. Fotedar, R. Nesper, *J. Power Sources* 278 (2015) 608-613.
- [10] X. Fan, Z. Li, A. Meng, C. Li, Z. Wu, P. Yan, *J. Mater. Sci. Technol.* 31 (2015) 822-827.
- [11] J. Wang, J.T. Chen, X.M. Yuan, Z.G. Wu, B.B. Miao, P.X. Yan, *J. Cryst. Growth* 286 (2006) 407-412.
- [12] Q. Zhou, Q. Lu, Y. Zhou, Y. Yang, X. Du, X. Zhang, X. Wu, *Surf. Coat. Technol.* 229 (2013) 135-139.
- [13] X. Li, Q. Bai, J. Yang, Y. Li, L. Wang, H. Wang, S. Ren, S. Liu, W. Huang, *Vacuum* 89 (2013) 78-81.
- [14] A.L. Ji, R. Huang, Y. Du, C.R. Li, Y.Q. Wang, Z.X. Cao, *J. Cryst. Growth* 295 (2006) 79-83.
- [15] X. Li, L.H. Hector, J.R. Owen, *J. Phys. Chem. C* 118 (2014) 29568-29573.