

Structural Characterization and Electrical Property of the Manganese Oxides/Silver Nanocomposite Thin Films

Yi Hu, Jiun-Shing Liu, and Tung-Cheng Liu

Abstract—The microstructural characterization and electrical properties of the manganese oxides/silver nanocomposite thin films are investigated by the conducting probe atomic force (CP-AFM). The nanocomposite thin films were obtained through electrodeposition by potentiostatic method with silver acetate ($\text{AgC}_2\text{H}_3\text{OOH}$) and potassium permanganate (KMnO_4) aqueous solution. The morphology for the thin films was examined by atomic force microscopy (AFM), Scanning Electronic Microscopy (SEM) and transmission electron microscopy (TEM). The spherical Ag_2O nanoparticles of several nanometer are dispersed homogeneously in the thin films and cubic shape Ag nanoparticles of about 100nm are spreaded on the surface of MnO_x thin film. The thickness of the MnO_x thin film is about 250nm. The schottky junction between Ag and MnO_x with rectifying behavior was evidenced by CP-AFM measurement. The turn-on voltage for the junction is around 0.69V.

Index Terms—Silver nanoparticles, manganese oxides, thin film, electrodeposition.

I. INTRODUCTION

Manganese oxides are widely used for energy storage devices due to low cost, high energy density, environment pollution free and nature abundance [1]-[3]. A lot of types of manganese oxides have been investigated, including nanocrystalline and amorphous phases [4]-[6]. In these oxides, MnO_2 thin films for the supercapacitive electrode exhibited a relative high specific capacitance (SC) of 700 F/g as reported [7], [8]. However, the SC of the MnO_2 electrode decreased with the increase of film thickness due to the poor conductivity of MnO_2 (10^{-5} - 10^{-6} Scm^{-1}) and limits the charge/discharge rate for high-power applications [9]. On the other hand, non-stoichiometric manganese hydroxide MnO_x also has good SC properties, and can be obtained by converting the manganese hydroxide ($\text{Mn}(\text{OH})_2$) [10], [11]. The $\text{Mn}(\text{OH})_2$ films can be fabricated by cathodic electrodeposition from Mn^{2+} salts solution.

Such a nanostructured film usually gives much higher energy storage density. The performance of the energy devices are basically determined by the structural and electrochemical properties of electrode materials. Nevertheless, the electrical capacity of supercapacitor cell depends on the electron transport mechanism and the type of series connection resistance of the cell. The resistance of the

electrode must be decreased to a proper value to give high electronic transport and low charge leakage.

In this study, the manganese oxides thin films were electrodeposited on the and ITO glass substrates with potassium permanganate solution by potentiostatic method. In addition, silver was added as the conduction drug to improve the conducting properties of the manganese oxides thin film. The potassium permanganate was adopted in this work is because that it is an oxidizing agent widely used as reported [12]. This would enhance to co-deposit Ag with the manganese oxides at the same side.

II. EXPERIMENTAL DETAILS

The electrochemical deposition and characterization of the thin films were conducted at room temperature using a Jichan 5000 electrochemical workstation in a standard cell with a platinum counter electrode, and a SCE or Ag/AgCl reference electrode. The thin films were electrochemically deposited on ITO glass substrate with potentiostatic method (-0.7V vs. open circuit) for 200s.

The solutions for the deposition are prepared with the potassium permanganate and silver acetate dissolved in deionized water. The concentration of potassium permanganate is 0.1M and the molar ratio of the Ag/Mn in the solution is 1.6%.

The morphology of the thin film was studied using a field emission scanning electronic microscope (FESEM, Hitachi 4800). The states of the ions were analyzed using an X-ray photoelectron spectroscopy (XPS, VG ESCA Scientific Theta Probe) under Al K α (1486.6eV) and the X-ray spot size is 15 μm . The surface morphology and the surface electrical properties were conducted by the AFM (Digital Instrument NS3a controller with D3100). Commercial sharpened PtIr₅ coating tips attached to triangular cantilevers were used. The set point was adjusted to minimize the force between the tip and the sample in each measurement.

The I-V characteristic of the sample was also measured by Conductive Atomic Force Microscopy (CP-AFM). CP-AFM was used to examine the surface morphology and electrical properties distributed of the films. Atomic force microscopy (AFM) is normally used to study the topography of substrates and structures made on them. Scanning of the sample is done with a sharp tip on a cantilever. If the cantilever and tip are made from of electrically conducting material, electrical properties of the films can be studied at the same time.

III. RESULTS AND DISCUSSION

Fig. 1 shows the SEM surface micrograph of the

Manuscript received January 5, 2013; revised March 4, 2013. This work was supported by National Science Council, Taiwan, ROC, under the grant NSC 99-2221-E-036-013.

The authors are with Department of Materials Engineering, Tatung University, Taipei, Taiwan, ROZ (e-mail: huyi@ttu.edu.tw, scottsym@yahoo.com.tw, emptylau@hotmail.com).

manganese oxides thin films. It was found that cubic shape particles and near-spherical smaller particles precipitated on the surface of the thin films. The size of the near-spherical particles was about 30~50nm and that of the cubic shape particles was about 100nm. The thickness of the MnO_x thin film is about 250nm. The composition of the particles on the thin films was identified as the Ag from the EDX investigation. (the left top in Fig. 1) The EDX spectrum of the sample shows the presence of Mn, Ag and O as the major elements at the vicinity of the cubic particles. In addition, peaks corresponding to Si and In from ITO glass substrates are also present. Therefore, the main composition of the cubic particles is Ag from EDX analysis.

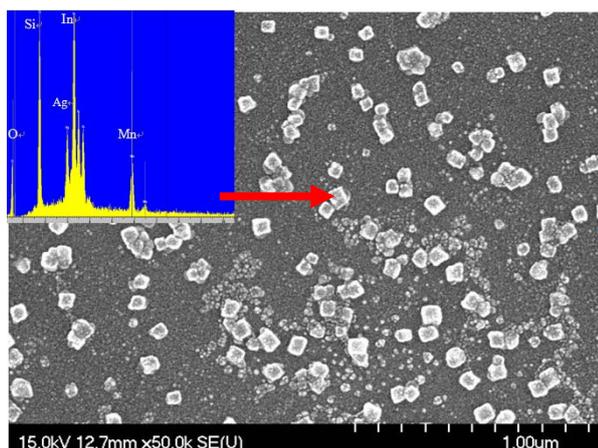


Fig. 1. The SEM micrographs of the thin films and the EDX spectrum of the particles (as arrowed)

Fig. 2 shows the TEM micrographs for the MnO_x matrix of the thin film. It was found that the MnO_x matrix has the near-spherical nanoparticles embedded into the films as in Fig. 2 (a). The size of the nanoparticles (darker particles) varied from several nanometer to 30nm. The typical diffraction pattern of spherical nanoparticles was shown in Fig. 2 (b). The diffraction pattern of the nanoparticles was classified as the single phase of Ag₂O with primitive FCC structure (JCPDF: 76-1393). On the other hand, the diffuse ringing diffraction pattern of the matrix indicates that the matrix MnO_x thin film is near amorphous as in Fig. 2 (c). This is well agreement to that the thin film is composed of the MnO_x nanoparticles of about 10nm from SEM observation.

On the other hand, Fig. 3 shows the TEM micrographs of the cubic particles, which dispersed on the surface of the MnO_x thin films. The main composition of the cubic shape particle is identified as metal Ag from the EDX spectra analysis as in Fig. 3. The spotty diffraction pattern suggests the nanoparticles of silver metal with FCC structure. This is well agreement to the result of SEM analysis. Therefore, the microstructure of the thin films is that the spherical Ag₂O nanoparticles of several nanometer are dispersed homogeneously in the thin films and cubic shape Ag nanoparticles of about about 100nm spreading on the surface of MnO_x thin film.

Fig. 4 shows the XPS spectrum of Mn2p_{3/2} of the thin film. The binding energy of the Mn2p_{3/2} for the manganese oxidation state is 640.9eV for the Mn²⁺, 641.9eV for the Mn³⁺, 642.5eV for the Mn⁴⁺ as reported in literature [13]. In our study, Therefore, the predominant phase of the thin film

is MnO₂ with small amount of Mn₂O₃. The manganese oxidation state of this film was 17.8 at% for Mn³⁺ and 82.2 at% for Mn⁴⁺ from evolution of the spectra.

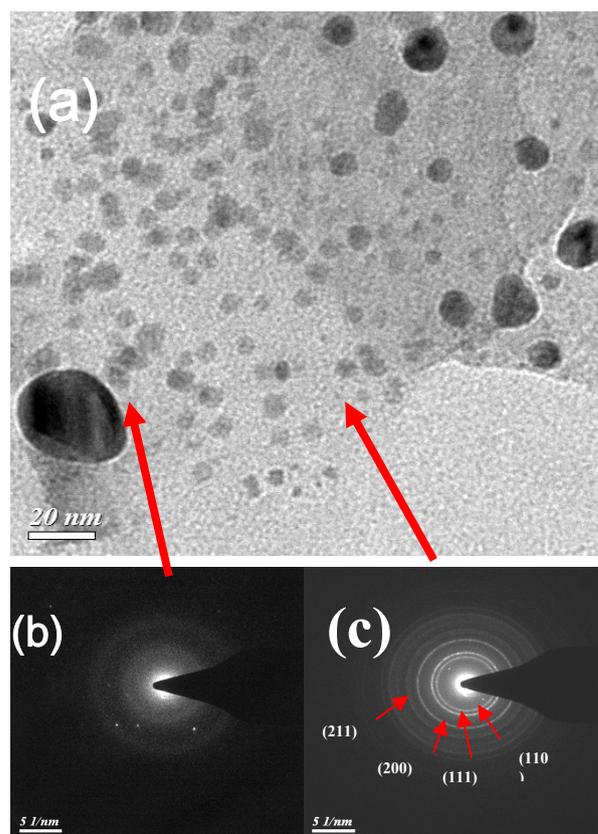


Fig. 2. TEM micrographs and electron diffraction patterns of the darker nanoparticles and MnO_x thin film matrix. The darker nanoparticles are identified as Ag₂O crystallites.

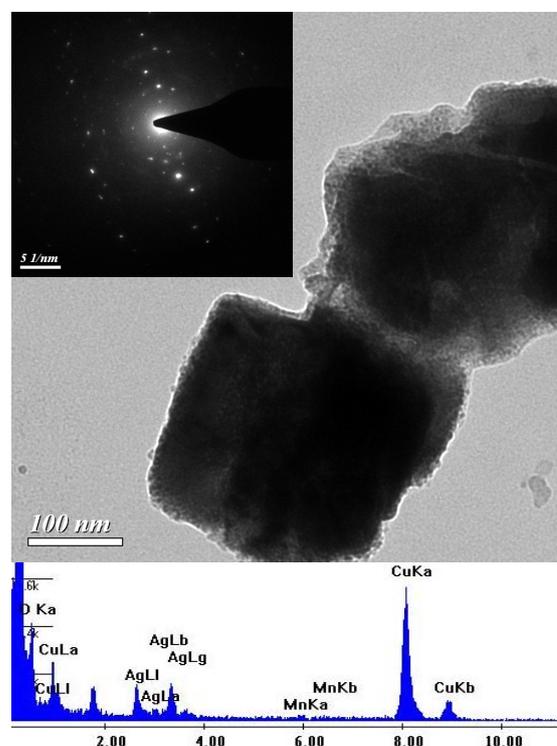


Fig. 3. TEM micrographs and electron diffraction pattern of the cubic shape particles

Fig. 5 shows the surface morphology and the surface electrical conducting imagines of the thin films, the with

lighter particles as observed in Fig (5.a) are Ag nanoparticles. The size of the particles is about 200nm measurement from AFM. This is very close to the observation from FESEM analysis.

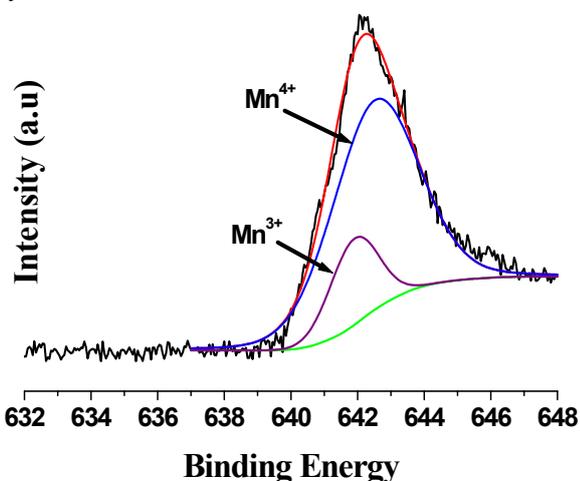


Fig. 4. The XPS spectra of Mn_{2p3/2} of the sample. This peak was divided into two spectra with Mn³⁺ and Mn⁴⁺.

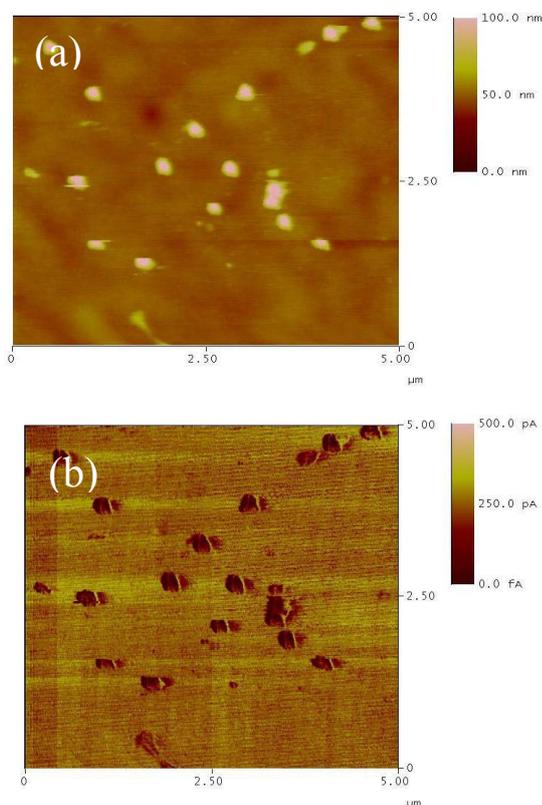


Fig. 5. Surface morphologies of the thin films scanned by the CP-AFM. (a) in normal mode, and (b) in conducting mode.

On the other hand, these Ag particles are darker spots from CP-AFM scanning as in Fig. 5(b). This is ascribed to the lower current through to Ag nanoparticles. The lower current through the Ag nanoparticles is primarily due to the metal-semiconductor contacts as Schottky barriers. A metal-semiconductor junction that does rectify current is called a Schottky contact. It has been reported that a saddle potential shape underneath the nano-Schottky contacts was considerably modified by the surface Fermi level pinning on the air exposed free surfaces [14].

This suggested that the potential underneath the Schottky

contact between the MnO_x matrix and silver particle is higher than that in the interior of the silver nanoparticles and MnO₂ matrix. The electrons in the silver nanoparticle with lower potential should overcome the Schottky barrier to transport. However, silver nanoparticles would become insulating if the applied field is lower than the Schottky barrier as seen in Fig. 5(b).

Fig. 6 shows the structure, current-voltage performance, of our device. It shows a typical forward $I-V$ characteristic of an Ag and MnO_x junction measured at 300 K. This $I-V$ characteristic shows the typical Schottky barrier behavior and confirms the explanation of the darker spots of Ag nanoparticles in Fig. 5 (b). The resistance of the Schottky barrier in the field emission regime is quite low as shown from the step increase in current at about 0.06V. It was measured by CP-AFM bias voltage with a step of 0.06V. The turn-on voltage for the sample, therefore, is around 0.69V from CP-AFM measurement. This Schottky behavior have a much faster response under forward bias conditions. This may be attributed to the highly conducting behavior of the MnO_x thin films and thus gives a low series resistance of the junction.

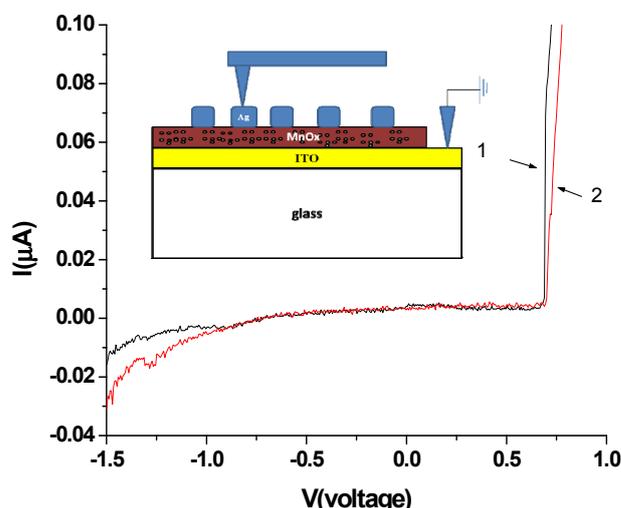


Fig. 6. The $I-V$ characteristics of the thin films measured by CP-FAM. The scan of the $I-V$ measurement was repeated twice. The number shown in figure indicates the first time and second time scanning.

IV. CONCLUSION

Manganese oxides/silver nanocomposite thin films were prepared by electrodeposited on ITO substrate. Silver particles of about 100nm spreaded on the surface of the MnO_x thin film, whereas the Ag₂O nanoparticles precipitated in the thin films. The thickness of the MnO_x thin film is about 25nm. Schottky barrier was obtained from the variation of electrical conducting behavior between the silver nanoparticles and MnO₂ matrix. The turn-on voltage for forward bias was obtained around 0.69V.

REFERENCES

- [1] S. Komaba, A. Ogata, and T. Tsuchikawa, "Enhanced supercapacitive behaviors of birnessite," *Electrochem Commun.*, vol. 10, pp.1435-1437, 2008.
- [2] R. N. Reddy and R. G. Reddy, "Sol-gel MnO₂ as an electrode material for electrochemical capacitors," *J. Power Sources*, vol. 124, pp. 330-335, 2003.

- [3] M. Toupin, T. Brousse, and D. Belanger, "Charge storage mechanism of MnO₂ electrode used in aqueous electrochemical capacitor," *Chem. Mater.*, vol. 16, pp. 3184, 2004.
- [4] C. C. Hu and T. W. Tsou, "Ideal capacitive behavior of hydrous manganese oxide prepared by anodic deposition," *Electrochem. Commun.*, vol. 4, pp. 105, 2002.
- [5] E. Beaudrouet, A. Le Gal La Salle, and D. Guyomard, "Nanostructured manganese dioxides: Synthesis and properties as supercapacitor electrode materials," *Electrochim. Acta*, vol. 54, pp. 1240, 2009.
- [6] M. S. Wu and P. C. J. Chiang, "Fabrication of nanostructured manganese oxide electrodes for electrochemical capacitors," *Electrochim. Solid-State Lett.*, vol. 7, pp. 123, 2004.
- [7] S. C. Pang, M. A. Anderson, and T. W. Chapman, "Novel electrode materials for thin-film ultracapacitors: Comparison of electrochemical properties of sol-gel-derived and electrodeposited manganese dioxide," *J. Electrochem. Soc.*, vol. 147, pp. 444, 2000.
- [8] S. C. Pang and M. A. Anderson, "Novel electrode materials for electrochemical capacitors: Part II. Material characterization of sol-gel-derived and electrodeposited manganese dioxide thin films," *J. of Mater. Res.*, vol. 15, pp. 2096, 2000.
- [9] X. Lang, A. Hirata, T. Fujita, and M. Chen, "Nanoporous metal/oxide hybrid electrodes for electrochemical supercapacitors," *Nature Nanotech.*, vol. 6, pp. 232–236, 2011.
- [10] N. Nagarajan, H. Humadi, and I. Zhitomirsky, "Cathodic electrodeposition of MnOx films for electrochemical supercapacitors," *Electrochim. Acta.*, vol. 5, pp. 3039, 2006.
- [11] N. Nagarajan, M. Cheong, and I. Zhitomirsky, "Electrochemical capacitance of MnOx films," *Mater. Chem. Phys.*, vol. 103, pp. 1, 2007.
- [12] D. Zhao, Z. Yang, L. Zhang, X. Feng, and Y. Zhang, "Electrodeposited manganese oxide on nickel foam-supported carbon nanotubes for electrode of supercapacitors," *Electrochim. and Solid-State Lett.*, vol. 14, no. 6, pp. A93-A96, 2011.
- [13] J. S. Foord, R. B. Jackman, and G. C. Allen, "An X-ray photoelectron spectroscopic investigation of the oxidation of manganese," *Philos. Mag.*, vol. A49, pp. 657, 1984.
- [14] T. Sato, S. Kasai, H. Okada, and H. Hasegawa, "Electrical properties of nanometer-sized schottky contacts on n-GaAs and n-InP formed by in situ electrochemical process," *Jpn. J. of Appl. Phys.*, vol. 39-7B, pp. 4609, 2000.



Yi Hu is the chairman in Department of Materials Engineering, Tatung University (TTU). Dr. Hu earned his BS and MS in Mechanical Engineering from TTU in Taiwan and his PhD degree in Materials Science and Engineering from the University of California, Los Angeles (UCLA) in USA. His research major is in the field of advanced ceramics and his PhD research involved developing

novel organic-inorganic hybrid materials through sol-gel method. Dr. Hu has worked in the field of electronic ceramics, glass-ceramics, and sol-gel technique for more than 20 years and has published more than 100 peer-reviewed journal articles, symposium articles, and industry reports in this field. He was a member of the Materials Research Society-Taiwan (MRS-T) and of the The Chinese Ceramic Society (Taiwan).



Jiun-Shing Liu was born in Tai-Chung, Taiwan. He received the BS degree in Materials Science and Engineering from the Feng Chia University (FCU) and MS in Materials Engineering from Tatung University (TTU) in Taiwan. He is currently a Ph. D. candidate Materials Engineering at TTU. His research interests include energy storage supercapacitor and electrochemical deposition technique, Sol-gel technique.



Tung-Cheng Liu was born in Taipei, Taiwan. He received the BS degree in Materials Science and Engineering from the Feng Chia University (FCU) and MS in Materials Engineering from Tatung University (TTU) in Taiwan. He is currently a Ph. D. candidate Materials Engineering at TTU. His research interests include solar cell technique, electrochemical deposition technique.