Surface Science 000 (2017) 1–6

Contents lists available at ScienceDirect

Surface Science

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

Effect of oxidation state of manganese in manganese oxide thin films on their capacitance performances

Zhiqiang Wang [a], Dongfang Yang [b,*], Tsun-Kong Sham [a,*]

[a] Department of Chemistry, University of Western Ontario, London, Ontario N6A 5B7, Canada
[b] Automotive and Surface Transportation Research Centre, National Research Council Canada, 800 Collip Circle, London, Ontario N6G 4X8, Canada

ARTICLE INFO

Keywords:
Manganese oxides
Pseudo-capacitor
X-ray absorption near edge structures
Amorphous
Oxidation states

ABSTRACT

Mn oxides, which are relatively low cost with low toxicity and environmental friendly, are regarded as one of the most promising candidate materials for pseudo-capacitors. The oxidation state of Mn ion in the oxides (e.g.: +2, +3, +4, +6 and +7) is a very critical factor affecting the specific capacitance. Three Mn oxide films (crystalline Mn_2O_3, amorphous Mn_2O_x, x ~ 3.74 and crystalline Mn_3O_4) with different oxidation states of Mn were prepared using a pulsed laser deposition (PLD) method, which show different capacitance performances (crystalline Mn_2O_3 film > amorphous MnO_x film > crystalline Mn_3O_4 film). X-ray absorption near edge structures (XANES) is applied to investigate the electronic structures of these films. Mn K-edge and $L_{3,2}$-dege XANES results confirm that the bulk of the amorphous MnO_x film is composed of MnO_2 and Mn_2O_3 with Mn^{4+}/Mn^{3+} ratio of about 3:1. Total electron yield (TEY) XANES at the Mn $L_{3,2}$-edge which is surface-sensitive, suggests that the amorphous film also contains some Mn_3O_4 on the surface, which is proposed to be the reason why the amorphous MnO_x film shows moderate pseudo-capacitance behavior in between the pure Mn_2O_3 and Mn_3O_4 films.

1. Introduction

Energy storage is vital for the utilization of clean and renewable energy. Energy storage devices make it possible to store solar and wind electricity then use it whenever it is needed, not just when it is produced. Among them, supercapacitors have attracted much attention for their applications in portable electronic devices, electric vehicles and backup power [1,2]. Pseudo-capacitor is one type of supercapacitors that store energy via fast surface redox reactions in additional to ion adsorption. Metal oxides with pseudo-capacitive behaviours (e.g.: RuO_2, Fe_3O_4 and MnO_2) typically have several redox states or structures and contribute to the charge storage via fast Faraday charge transfer between different redox states [3, 4]. The remarkable performance of RuO_2 in supercapacitors (theoretical capacitance of 2000 $F{\cdot}g^{-1}$) has stimulated many interests in investigating metal oxide systems for supercapacitor applications [5-9]. The commercial use of RuO_2, however, is limited owing to its high cost and toxic nature. Mn oxides, which are relatively low cost, low toxicity, and environmental friendly, are regarded as one of the most promising alternatives among the less expensive metal oxides to RuO_2 for pseudo-capacitors (the specific capacitance of MnO_2, as high as 1300 $F{\cdot}g^{-1}$, has been reported [10]). Manganese commonly occurs in five different oxidation states: +2, +3, +4, +6 and +7. The oxidation state of Mn ion in the oxides is a very critical factor affecting the specific capacitance [11-14]. The pseudo-capacitive performance of Mn oxides is also affected by their microstructures and surface morphologies that are controlled by their fabrication methods and processing conditions [15].

As one of the physical vapor deposition processes, pulsed laser deposition (PLD) is very suitable for the fabrication of Mn oxides of different phases and valence states due to its flexibility and easiness in controlling the deposition process parameters such as substrate temperatures and oxygen gas pressures. Previous work has demonstrated that pure crystalline phases of Mn_2O_3 and Mn_3O_4 as well as amorphous phase of MnO_x can be successfully fabricated by proper selection of PLD processing parameters [14]. Pseudo-capacitive behaviors of these different phases and valence states of Mn oxides were evaluated by the electrochemical measurement in aqueous electrolyte and the results show that crystalline Mn_2O_3 phase has the highest specific current and capacitance (210 F/g at 1 mV/sec scan rate), while the values for crystalline Mn_3O_4 films are the lowest [14]. The specific current and capacitance values of the amorphous MnO_x films are lower than Mn_2O_3 film but higher than Mn_3O_4 film. Clearly, there are needs to get a better understanding of the fundamental reasons causing the difference in pseudo-capacitive behaviors of Mn oxide films with different phases and valence states, particularly for the amorphous MnO_x film.

X-ray absorption near edge structures (XANES) probes the local structure and bonding of the absorbing atom by monitoring the absorp-

* Corresponding author.
E-mail addresses: zwang443@uwo.ca (Z. Wang), dongfang.yang@nrc.gc.ca (D. Yang), tsham@uwo.ca (T.-K. Sham).

https://doi.org/10.1016/j.susc.2017.12.011
Received 22 November 2017; Received in revised form 18 December 2017; Accepted 19 December 2017
Available online xxx
0039-6028/

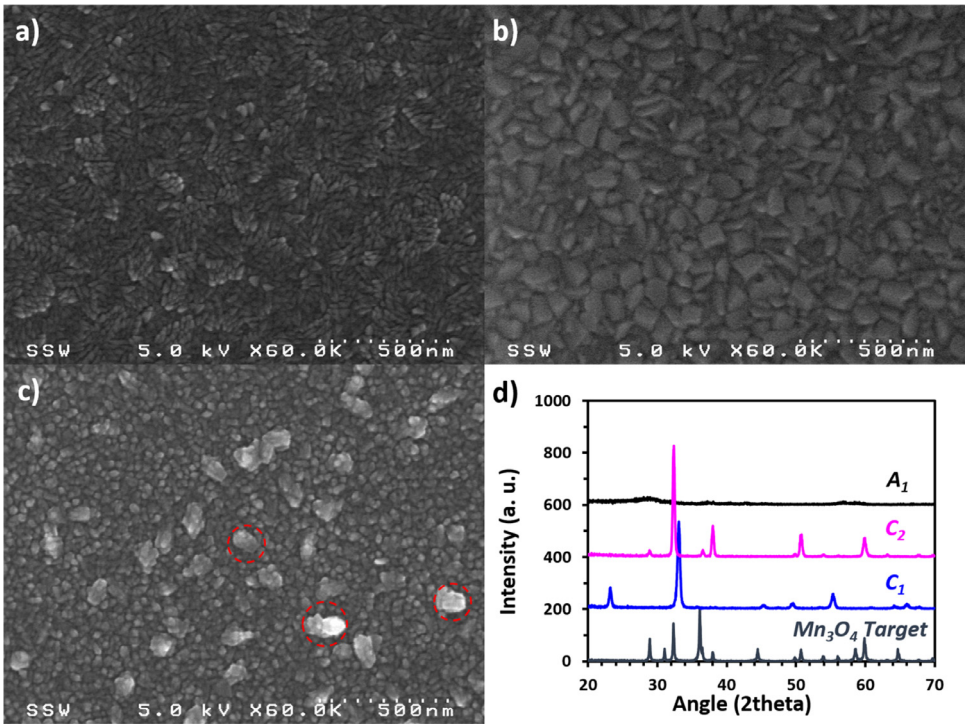

Fig. 1. (a)-(c) SEM images and (d) XRD patterns of manganese oxide films deposited on Si (1 0 0) substrates by PLD. (a) Sample C_1 (crystalline Mn_2O_3), (b) sample C_2 (crystalline Mn_3O_4) and (c) sample A_1 (amorphous MnO_x).

tion coefficient using tunable X-ray from a synchrotron light source, and can provide information on oxidation state, coordination, and symmetry of the atom of interest in a chemical environment [16]. XANES is an appropriate tool for the structural analysis of both ordered (crystalline) and disordered (amorphous) materials since it is a local probe and atomic-specific [17,18]. XANES also provides quantitative information of mixed-phase materials. The edge jump of the XANES spectrum is proportional to the quantities of the sample; the compositional fractions of the mixed-phase materials can be obtained by a linear combination fitting (LCF) of the spectra of their components [19,20]. Additionally, XANES has the unique ability to discern surface and bulk signals using total electron yield (TEY) and X-ray fluorescence yield (FLY), respectively, when surface and bulk have different compositions [17,21]. The electrons with relatively low kinetic energy have relatively short inelastic free mean path, while the fluorescence X-ray has a much longer attenuation length in solids, typically two orders of magnitude longer in the soft X-ray region than the probing depth of Auger electrons [22]. Therefore, XANES is a powerful tool in the characterization of materials, especially mixed-phase amorphous materials.

In this work, we report an investigation of the electronic structure of Mn oxides films of different phases and valence states using XANES at the Mn K-edge and $L_{3,2}$-dege. XANES results helped us characterize these films, especially amorphous MnO_x films, and further understand the effect of the Mn oxidation state in Mn oxides films on their capacitance performances.

2. Experimental

2.1. PLD of manganese oxide thin films

Manganese oxide thin films were grown on silicon wafers using PLD technique. Detailed information about the deposition processes can be found elsewhere [14]. Briefly, a 3.5-inch Mn_3O_4 disk (99.9%, K. J. Lesker) was used as the target, and a 3-inch Si (100) wafer (p-type, $\rho = 10–30\ \Omega\cdot cm$, Polishing Corporation of America) or a 20 mm × 30 mm × 1.0 mm polished rectangular stainless steel 316 substrate was used as the substrate. Before the deposition, the system was pumped down to a base pressure below 3×10^{-7} Torr using a turbomolecular pump. During the PLD process, a laser beam generated by a KrF excimer laser (Lambda Physik LPX-210i) with a wavelength of 248 nm and pulse duration of 25 ns was introduced into the deposition chamber and focused onto the target surface. The laser fluency on the target was adjusted to be 2–3 J/cm^2, while the repetition rate was fixed at 50 Hz. To improve the film homogeneities, the substrate was rotated along the vertical axis at a speed of 35 rpm. As shown in Table 1, three manganese oxide thin films (C_1, C_2 and A_1) were synthesized with different substrate temperatures and oxygen pressures.

Table 1
Synthesis conditions of different Mn oxide films (*characterized by XRD).

Sample ID	Target	Substrate temp.	O_2 pressure	Phase*
C_1	Mn_3O_4	500 °C	100 mTorr	Crystalline Mn_2O_3
C_2	Mn_3O_4	500 °C	1 mTorr	Crystalline Mn_3O_4
A_1	Mn_3O_4	200 °C	100 mTorr	Amorphous MnO_x

The film structure was examined by X-ray diffraction equipment (XRD, Philips, X-Pert MRD) with Cu Kα radiation. The surface morphology was characterized by field emission scanning electron microscope (FE-SEM; Leo 440).

2.2. XANES measurement

Mn K-edge XANES measurements were performed in FLY mode on sector 20 BM-B of the Advanced Photon Source (APS) and SXRMB beamline of the Canadian Light Source (CLS). The absorption energy was calibrated using Mn metal as reference (6537.67 eV). FLY spectra were normalized to the incident photon flux (I_0) recorded by the ionization chamber. Mn $L_{3,2}$-edge XANES was measured in both TEY and FLY mode on the SGM beamline of CLS. The TEY was detected with the specimen current and the FLY was measured by detecting the X-ray fluorescence photons via silicon drift detectors (SDD). XANES spectra were normalized to the incident photon flux monitored with a refreshed Au grid.