Plasma Enhanced Atomic Layer Deposition for Conformal Coating of Manganese Oxide on Carbon Nanowalls

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Abstract: Carbon nanowalls (CNWs) coated with manganese oxide (MnO_x) are potential supercapacitors. This study discusses the conformal coating of MnOx on CNWs using PEALD process to improve the disconformity issues. $Mn(thd)_3$ was used as a manganese source and O_2 remoto plasma was used for a oxidizing media to cover CNW with MnOx conformally at 395 K. The film growth rate was achieved 5pm/cycle. The deposited MnO_x thin film conformity was confiremed by Backscattering electrons (BSE) scanning microscopy and energy-dispersive X-ray spectroscopy (EDS) analysis after 1000 and 5000 cycles of ALD.

Keywords: Plasma enhanced atomic layer deposition, carbon nanowalls, manganese oxide

1. Introduction

There has been a growing interest in high-performance electrode materials for electrochemical energy storage and conversion devices[1]. Carbon nanowalls (CNWs) consisting of innumerous vertically-aligned, two-dimensional thin walls have been very promising materials because of catalyst-free, environmental-friendly processing routes. Investigations have yet indicated that composite electrodes, e.g., carbon material plus metal oxide, have higher conductivity and lower volume expansion than conventional metal oxides. Conformal deposition of metal oxide on the intricate CNWs is challenging due to their high aspect ratio and narrow inter-wall gaps limiting the conformal deposition on conventional deposition methods such as Chemical vapor deposition (CVD) and Electrochemical deposition. Therefore, it remains still controversial to find a more suitable process for conformal coating of metal oxides on CNWs. As a subclass of the CVD, atomic layer deposition (ALD) has successfully been applied for conformal coating of metal oxides on different types of materials .Compare to CVD that all the reactants introduced to the substrate surface all at the same time, in ALD reactants introduced one after another to the reactor chamber and reacts with substrate surface with the advantages of conformity, thickness control of the deposited film. However, ALD requires high temperature for film deposition and in this case, plasma enhanced atomic layer deposition (PEALD) allows to lower the substrate temperature by keeping the thickness control, conformity at surface areas[2-4]. Nilsen et al (2003). applied thermal ALD technique for deposition of MnO_2 ,but they noted due to the reactants catalytic effect, it is challenging to make a conformal film deposition [5]. To the best knowledge of authors, the PEALD method has not been applied for conformal MnOx deposition on CNWs yet.To this end, the aim of this study is to present the conformal deposition of MnO_x on CNWs using PEALD. The conformal coating of MnOx on CNWs was confirmed using dedicated backscattering electron microscopy and energy-dispersive X-ray mapping (EDS) anlysis respectively.

2. Experimental procedure

A CO/H_2 microwave power discharge, plasma-enhanced chemical vapor deposition (PECVD) system with a 2.45 GHz microwave power supply was used to synthesize CNWs for 30s, as presented in the previous study [6]. Silicon wafers with dimensions of 9×9×0.5 (mm) were utilized as a substrate for synthesis of CNWs and subsequent deposition in the PEALD process.

The atomic layer deposition of manganese oxide film on CNWs was performed in a custom-made PEALD reactor, operated in an average pressure of 30 Pa as shown in Fig.1. As an oxygenation gas, O_2 was introduced at a flow rate of 6 sccm into the reactor chamber along with plasma discharge. Consequently, oxygen plasma was generated at a supply voltage of 9 kV. As a metal precursor, Tris (2,2,6,6-tetramethyl-3,5-heptanedionato) manganese, $Mn(thd)_3$, was held in a stainless-steel chamber at 395 K. Cyclic ALD process was performed by a valve operation controlled by ARDUINO (APPLIED SCIENCE AND TECHNOLOGY, INC AX2000). For a series of experiments, the response time of each cycle was set to 0.5, 1.5, 4 and 8 s. Each cycle of the ALD process consists of repeating four steps: (1) precursor injection, (2) evacuation, (3) oxygenation, and (4) evacuation.The substrate temperature was maintained at 460 K with the electrical heater inside the substrate stage and and MnOx films were grown on the CNWs/Si substrate for 1000 and 5000 Cycles of ALD at a fixed substrate temperature of 460 K. Table 1 summarizes the optimum experimental conditions of PEALD of MnOx deposition.

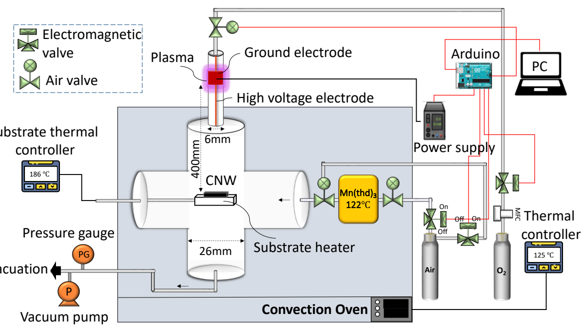

Fig.1. PEALD experimental setup diagram

Table 1. Selected experimental conditions of PEALD

Substrate	CNW/Si
Precursor feed rate [mg/min]	0.14
O_2 flow rate [sccm]	6.0
Substrate temperature [°C]	186
Pressure [Pa]	30, 25, 35, 25

Field-emission gun scanning electron microscopes (FEG-SEMs), equipped energy-dispersive X-ray spectrometry (EDS) detector were used for observations and elemental analysis of the samples.

3.**Results and discussion**

Fig.2a shows secondary electron (SE) SEM micrographs of the of CNWs grown for 30 s to a thickness of about 1.5 μm, at a growth rate of ca. 3 μm/min, as reported in detail previously [6]. Fig.2b and Fig.2c demonstrate the MnO_x /CNWs samples after 1000 and 5000 ALD cycles, respectively. Thickening of CNWs with blunted edges is clearly observed in the top surface of the sample treated for 5000 cycles, which demonstrates the deposition of overlay material during the ALD. The overlay deposits thoroughly on the CNWs with the shape of nanowalls left intact. The average thickness of the MnO_x /CNWs composite layer was measured about 53.84 nm in the sample coated for 5000 cycles. Ignoring the thickness of internal CNW in the composite and account for equal coating thickness on either side, the growth rate MnO_x can be estimated 5 pm per cycle.

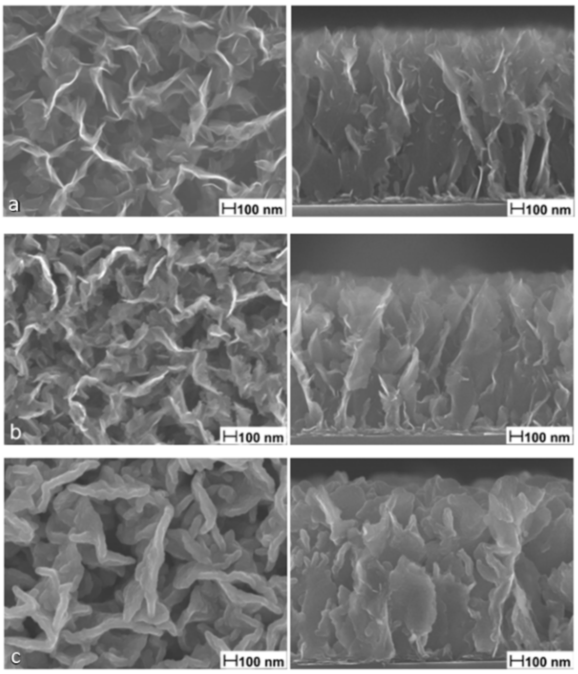

Fig.2. SEM (secondary electron) images from the top surface of CNWs grown on the Si substrate for 30 s (a), MnO_x/CNWs grown for 1000 ALD cycles (b), MnO_x/CNWs synthesized for 5000 ALD cycles (c). In each row, the right frame shows corresponding cross-section.

Fig.3 compares the SE micrographs with backscattering electrons (BSE) scanning microscopy of the cross-sections of the as-grown CNWs and those coated with MnO_x for 1000 and 5000 ALD cycles. CNWs band is not identified in the as-grown CNWs, faintly detected in the sample treated for 1000 cycle but well clearly illuminated in the sample treated for 5000 cycles in BSE images. Manganese atoms enhance the pixel intensity due to the higher backscattering coefficient compare to carbon and oxygen atoms[7]. Therefore, sufficient intensity has missed for the as-grown CNWs due to negligible backscattering coefficient of C atoms while the Mn and O atoms have created strong intensity out of the thick MnO_x overlay on the sample treated for 5000 cycles.As rationalized in the following, BSE imaging clarifies a conformal coating of MnO_x on CNWs. The SE images are almost identical in brightness with negligible alteration by ALD cycles. The through-thickness brightness confirms the conformal deposition of MnO_x on CNWs during ALD.

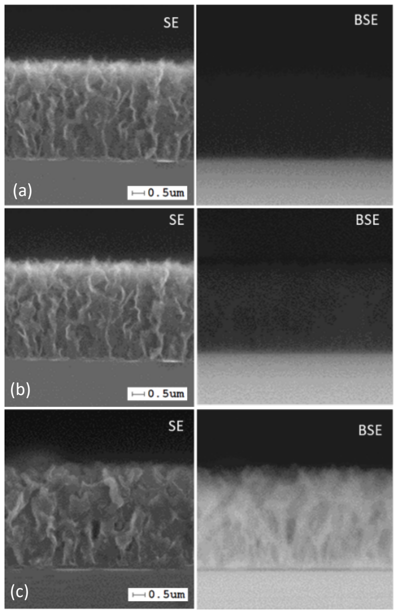

Fig.3. Secondary electrons (SE) and backscattered electrons (BSE) micrographs of the cross-section of as-grown CNWs (a), and the samples coated with MnO_x for 1000 (b) and 5000 (c) ALD cycles.

Additional proof of the conformal coating of MnO_x on CNWs was provided using characteristic X-ray (Kα lines) elemental mapping by the EDS. Fig.4 represents elemental maps corresponding to the cross-sections of as-grown CNWs and the samples coated with MnO_x for 1000 and 5000 cycles. The intensity of C map is comparable in all samples. However, Mn map intensifies considerably in the samples coated during 1000 and 5000 ALD cycles. For O map, one may compare the differential intensity of CNWs band with Si substrate considering the higher noise, to come into the same conclusion. Therefore, these maps indicate the conformal coating of MnO_x on the CNWs. Interestingly, EDS represents higher sensitivity than BSE imaging considering the clear Mn mapping of the sample coated for 1000 cycle.

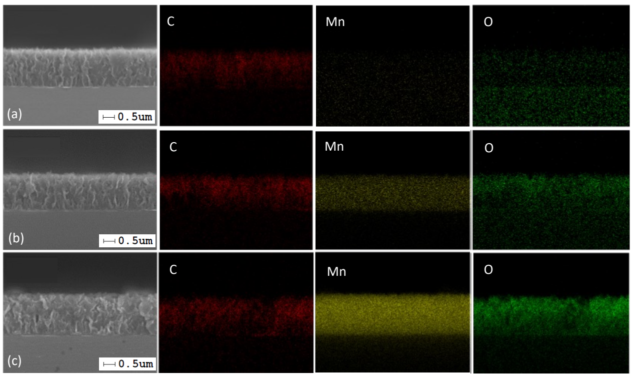

Fig.4. Secondary electrons (SE) micrographs with corresponding EDS elemental maps showing the distribution of C, Mn and O atoms in the cross-section of as-grown CNWs (a), and the samples coated with MnO_x for 1000 (b) and 5000 (c) ALD cycles.

4. Conclusion

Due to its conformal and film thickness control charchteristic, in this study we demonstrate a promissing PEALD process for MnO_x depostion on CNWs based on $Mn(thd)_3$ precursor. The GPC for the ALD process was revealed 5 pm/cycle from FE-SEM images. EDS and BSE results was indicate that despite the difficulty of conformal deposition on the surface of CNWs due to their inertness, high aspect ratio, and highly active edges, a uniform distribution of Mn and O atoms was achieved after 1000 and 5000 cycles of ALD. This study provides a new pathway for incresing the conformity of metal oxides on CNWs and their future application for electrochemical enrgy/storage electrode materials.

5.References

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