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Synthesis of electro-active manganese oxide thin films by plasma enhanced chemical vapor deposition

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ABSTRACT

The good stability, cyclability and high specific capacitance of manganese oxide (MnO_x) has recently promoted a growing interest in utilizing MnO_x in asymmetric supercapacitor electrodes. Several literature reports have indicated that thin film geometries of MnO_x provide specific capacitances that are much higher than bulk MnO_x powders. Plasma enhanced chemical vapor deposition (PECVD) is a versatile technique for the production of metal oxide thin films with high purity and controllable thickness. In this work, MnO_x thin films deposited by PECVD from a methylcyclopentadienyl manganese tricarbonyl precursor are presented and the effect of processing conditions on the quality of MnO_x films is described. The film purity and oxidation state of the MnO_x films were studied by Fourier transform infrared spectroscopy and X-ray photoelectron spectroscopy. Preliminary electrochemical testing of MnO_x films deposited on carbon fiber electrodes in aqueous electrolytes indicates that the PECVD synthesized films are electrochemically active.

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1. Introduction

Interest in utilizing the pseudocapacitive properties of manganese oxide (MnO_x) in electrochemical capacitors has grown significantly over recent years. MnO_x offers good specific capacitance and is an inexpensive and non-toxic alternative to ruthenium oxide. Further, when MnO_x is deposited as a thin film, several literature reports indicate that very high gravimetric capacitances can be obtained (up to 10 times greater than what is observed for electrodes based on bulk MnO_x powders) [1,2]. The origin of capacitance improvement for thin film MnO_x electrodes is believed to be related to the poor electrical conductivity of bulk MnO_x and the relatively short diffusion lengths for cation transport in thin film electrodes [3].

MnO_x thin films have been produced by many techniques including electrodeposition [3–6], dip coating in MnO_x sols [7,8] followed by calcinations [4] or annealing/pyrolysis [9], hydrothermal synthesis [10], oxidative-soak-coating [11], solution gelation (sol–gel) [12], successive ionic layer adsorption and reaction [13], thermal evaporation [14], reactive sputtering [15], oxygen plasma assisted molecular beam epitaxy [16], thermally driven chemical vapor deposition (CVD) [17,18], pulsed laser deposition [19] and atomic layer deposition [20,21]. These deposition techniques produce MnO_x films with a wide range of Mn oxidation states, crystallinities, densities, and morphologies. As the capacitive properties of MnO_x films are often highly dependent on the physical properties of the thin film [19], much work continues to be devoted to understanding the requisite film properties for optimum electrochemical

performance. Efforts to produce films with controlled oxidation states, crystallinity and surface morphology using a variety of synthesis techniques should help to further elucidate the complex structure–property behaviors of electroactive MnO_x films.

In this report, plasma enhanced chemical vapor deposition (PECVD) is explored as a method to deposit manganese oxide thin films. PECVD is a versatile technique for the production of metal oxide thin films [22] that yields films with controllable thickness and good purity. It is especially attractive for producing well-adhered films on a variety of substrates materials with complex shapes and/or high aspect ratios since the thin film coating is applied by ion bombardment. The ability of PECVD to apply MnO_x coatings on high surface area substrates is of specific interest for thin film electrode fabrication since maximization of the MnO_x surface area increases the area available for cation exchange and minimizes diffusion distances [12]. PECVD is also a microelectromechanical systems compatible fabrication technology that could offer the in-place fabrication of thin film batteries/capacitors onto electronic components. Despite the apparent suitability of PECVD for producing MnO_x thin films for electrochemical applications, there are no previous literature reports of PECVD synthesized MnO_x films. PECVD also provides some unique advantages over some of the other MnO_x synthesis techniques. Many of the wet chemistry techniques (e.g. electrodeposition) cannot produce fully-dense, conformal coatings of metal oxide on high aspect ratio structures [14] and physical vapor deposition methods such as thermally driven CVD mandate the use of high temperatures. Since the plasma source serves as the driving force for chemical reactions, PECVD can be carried out at very low temperatures enabling the usage of a wide variety of substrate materials.

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Additionally, the low temperature synthesis of MnO_x may be advantageous for producing amorphous MnO_x (rather than crystalline MnO_x) which is more commonly employed for electrochemical applications [13].

In the following sections, the synthesis of MnO_x thin films by PECVD is described. Although the PECVD synthesis of closely related metal oxide thin films has been previously described (e.g. lithium manganese oxide [23]), the PECVD synthesis of pure MnO_x films has not appeared in the literature. A design of experiments approach was used to explore the effect of PECVD process variables on the properties of MnO_x films. The physical properties of the MnO_x films were evaluated using Fourier transform infrared (FTIR) spectroscopy, X-ray photoelectron spectroscopy (XPS) and spectrophotometry. Preliminary characterization of the electrochemical performance of the PECVD synthesized MnO_x films is also presented; single electrode experiments indicate that PECVD deposited MnO_x is electrochemically active.

2. Experimental

The PECVD system was designed and built by Innovative Systems Engineering, Inc. (model number ISE-OE-PLA-1000). 2 round electrodes, 34.3 cm in diameter, are spaced 40 mm apart in the deposition chamber. The top electrode is powered by a 40 kHz radio-frequency power supply. A Baratron pressure gauge connected to the deposition chamber provides pressure monitoring during plasma processing and a vacuum throttling valve enables dynamic control of the chamber pressure. Process gases (argon, oxygen and hydrogen, >99.9995% purity, Praxair) are independently controlled by mass flow controllers (MFCs). (Methylcyclopentadienyl)manganese(I) tricarbonyl (MMT, >88% purity, Sigma Aldrich) was used as the manganese source. MMT is a volatile liquid at room temperature therefore a vapor feedstock of MMT was generated by bubbling argon gas through a heated (50 °C) MMT liquid reservoir. An MFC was used to regulate the flow rate of the argon carrier gas. All lines feeding MMT vapor into the deposition chamber were resistively heated to prevent condensation of the MMT vapor. The molar flow rate of the MMT precursor was calculated by using volumetric flow rate of the argon carrier gas and the saturated vapor pressure of the MMT precursor at 50 °C (the temperature of liquid MMT precursor reservoir). The saturated vapor pressure (P_{vap}) of the MMT precursor at 50 °C was obtained from the Antoine equation $[\log_{10}P_{vap} = A - (B / (T + C))]$. The Antoine parameters (A, B, C) were generated by fitting available literature data for the vapor pressure of MMT over a temperature range of 20 °C–100 °C [24–27]. The Antoine parameters for MMT were calculated to be 14.704, 8100.728, and 212.150, which yield vapor pressure in units of mm Hg and require temperature in units of Kelvin. The process gases, including MMT vapor, flowed into the deposition chamber through a shower head gas diffuser mounted on the top electrode. A temperature controlled closed water–glycol liquid loop was used to maintain the chamber and substrate pedestal at a constant 30 °C during PECVD deposition. Full automation of the deposition process (including regulation of chamber pressure, gas flow rate, and substrate temperature) is enabled by programmable logic controllers and a computer implementing CIMPLICITY (CimView, version 6) software.

A variety of substrates were utilized for PECVD experiments to facilitate film characterization and electrochemical studies. Substrates included glass cover slips (borosilicate glass, Thermo Scientific), silicon wafers (University Wafer), and carbon fiber papers (20 g/m², Technical Fibres). An acetone rinse was used to clean the glass and silicon substrates prior to MnOx deposition; the carbon fiber papers were used as received. The chemical composition of the MnOx films was analyzed by FTIR (Perkin Elmer Optical) and XPS (Kratos Analytical Axis Ultra Instrument). The transmittance of the films was determined by spectrophotometer (Thermo Scientific, Spectronic 200) in order to provide a relative measure of the film thickness. In some cases, ellipsometry (Gaertner L116C Variable Angle Ellipsometer) was used to obtain a precise measure of film thickness. The electrochemical performance of the

MnO_x thin films was evaluated by cyclic voltammetry (CV) experiments using a Gamry Potentiostat/Galvanostat. MnO_x coated carbon fiber papers were used as the working electrode while a platinum wire and Ag/AgCl electrode were used as counter and reference electrodes, respectively. The electrolyte was aqueous 2 M calcium chloride ($CaCl_2$); the pH of the aqueous electrolyte solution was adjusted to 7. Cyclic voltammograms were measured over scan rates of 2–1000 mV/s and a scan range of 0 to 1.0 V vs Ag/AgCl for up to 10 cycles.

3. Results and discussion

A methodology to deposit MnOx films by PECVD from a MMT precursor in the presence of oxygen, hydrogen and argon was developed. The high vapor pressure of MMT enables facile production of vapor feedstock for the PECVD chamber and since MMT has been utilized as a common gasoline additive, it is still relatively inexpensive and commercially available. Hydrogen was selected as a process gas since previous studies on the PECVD production of vanadium oxide, a related metal oxide, indicated that hydrogen scavenged free chlorine atoms generated by the vanadium oxytrichloride ($VOCl_3$) precursor and resulted in improved vanadium oxide deposition rates [28]. However, later studies by a different research group were unable to verify improvement of vanadium oxide growth rates by the addition of hydrogen process gas [29]. Although the literature on the potential of hydrogen to improve the metal oxide deposition rates (presumably by scavenging free organic species in the case of the MMT precursor) is conflicted, H_2 was included as a process variable in this investigation.

Initial PECVD studies focused on producing measurable deposition of MnO_x on glass and silicon wafer substrates. The chamber and substrate temperatures were maintained at 30 °C during deposition. The flow rate of MMT precursor was held constant at 4.5×10^{-7} mol/min. The volumetric flow rates of the process gas (Ar = 70–90 sccm, H_2 = 10–125 sccm, O_2 = 75–150 sccm) were set at relatively high values to encourage maximum deposition rates at the expense of process efficiency. The chamber pressure was maintained at a sufficient pressure (53–93 Pa) to ensure interaction between ions and gas precursor species without significant generation of unwanted particulate contaminants. The plasma power was gradually increased until the deposition of MnO_x thin films was observed. Deposition for a time period of 10 min with plasma powers of 25–300 W did not produce any MnO_x films detectable by visual inspection or scanning electron microscopy with energy dispersive spectroscopy analysis. When the plasma power was increased to 500 W, MnO_x films were visually observable on glass and silicon wafers after the 10 minute deposition period. PECVD-synthesized MnO_x films appeared as a transparent brown film when deposited on glass coverslips as shown in Fig. 1. Ellipsometry was conducted on a MnO_x film deposited on a silicon wafer for a time period of 60 min using a plasma power of 500 W, a chamber pressure of 80 Pa, a MMT molar flow rate of 4.5×10^{-7} mol/min (in Ar carrier), an O_2 flow rate of 125 sccm and an H_2 flow rate of 25 sccm. The thickness of the MnO_x film prepared using these unoptimized deposition conditions was measured to be 20 nm, yielding a deposition rate of

Fig. 1. PECVD synthesized MnO_x film (on left) coated on a glass cover slip and an uncoated glass cover slip (right).