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Low-temperature atomic layer deposition of crystalline manganese oxide thin films

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We present a new low-temperature atomic layer deposition (ALD) process based on Mn(thd)3 and ozone as precursors to fabricate crystalline α-MnO2 and Mn3O4 thin films; the phase composition is controlled by the deposition temperature such that the former phase forms in the range 60–100 °C and the latter in the range 120–160 °C. In both cases an appreciably high growth rate of ~1.2 Å/cycle is achieved. The spinel-structured MnO2 films are shown to be ferrimagnetic with the transition temperature determined at ~47 K.

Introduction

Manganese oxides form an interesting family of functional materials with a variety of attractive properties. These materials are already found in several important applications, and actively considered for a number of potential next-generation applications related to e.g. catalysis, batteries and supercapacitors. Moreover, manganese is more abundant and environmentally friendlier than most of the other transition metals. Manganese forms oxides such as MnO, Mn2O3, MnO2 and MnO4 with different oxidation states and with a number of polymorphs. For example, the tetravalent manganese oxide MnO2 performs differently in electrochemical and catalytic applications depending on its crystal structure, i.e. whether it exists in the form of α, β, γ, δ, ε or λ phase. One of the practical challenges is to fabricate the manganese oxide materials with the desired Mn oxidation state and the specific crystal structure, and also to engineer these materials into different application-required nanostructures. In particular, there is an increasing demand for high-quality thin films due to the development of microsystems. Electrodeposition, electrophoresis, dip coating, sol-gel methods, chemical vapour deposition (CVD), and atomic layer deposition (ALD) have been utilized for the deposition of manganese oxide thin films.

Among the different thin-film deposition techniques, ALD with its unique film growth mechanism based on self-limiting surface reactions between alternately introduced gaseous precursors is superior to the other techniques regarding the film uniformity and conformity. In spite of the increasing demand for techniques capable of producing high-quality manganese oxide thin films on various substrate architectures and the fast development of the ALD technology in general, only a few ALD processes for the growth of manganese oxides have been reported thus far. In these processes, only two different manganese precursors have been utilized, namely Mn(thd)3 (thd = 2,2,6,6-tetramethylheptane-3,5-dionate) with O3 as the oxygen source and Mn(CpEt)2 (CpEt = ethylcyclopentadienyl) combined with H2O. The former Mn(thd)3+O3 process yields crystalline MnO2 films, with the growth-per-cycle (GPC) values of ~0.2 Å/cycle within the deposition temperature window from 138 to 210 °C. With the latter Mn(CpEt)2+H2O process, MnO films with considerably higher GPC values of ~1.1 Å/cycle at 100–150 °C and 0.84 Å/cycle at 170 °C have been grown. Besides these conventional thermal ALD processes, three plasma-enhanced PE-ALD processes with ammonia, hydrogen and water plasma were recently developed based on the Mn(thd)3 precursor; most importantly, the different activated reactant gases utilized in these processes allowed the control of the oxidation state of manganese in the films. The GPC values reached were somewhat low though, e.g. ~0.2 Å/cycle with the ammonia plasma in the temperature window of 150 to 255 °C.

In this work, we employ for the first time a new zero-valent manganese precursor, manganese carbonyl Mn2(CO)10, for the low-temperature deposition of crystalline Mn3O4 and Mn12O19 thin films with the appreciably high growth rates of up to ~1.5 Å/cycle. Moreover, we demonstrate the successful control of the phase composition from Mn3O4 to Mn12O19 of the films by adjusting the deposition temperature. For the spinel-structured Mn3O4 films we also report the results of preliminary magnetic-property measurements.
Results and discussion

Our Mn$_2$(CO)$_{10}$+O$_3$ process yielded visually homogeneous thin films within the entire deposition temperature range of 60–200 °C studied. With deposition temperatures higher than 200 °C, the reaction turned out to be of the CVD type, and the films were notably rough. The controlled/constant deposition rate is arguably the most important feature of an ideal ALD process. Hence, saturation of the surface reactions was the first issue investigated here as well. In Fig. 1 we show the variation of the GPC value with varied precursor pulse lengths for our manganese oxide thin films deposited from Mn$_2$(CO)$_{10}$ and O$_3$ at 80 °C. At this relatively low deposition temperature the maximal GPC value of ~1.2 Å/cycle is obtained with a Mn$_2$(CO)$_{10}$ pulse length of 2 s; for the longer pulse lengths the GPC value remains the same, and even for the Mn$_2$(CO)$_{10}$ pulse length as short as 1 s the resultant GPC value is only slightly lower. Also for the O$_3$ pulse, the pulse length of 2 s was found sufficient to achieve the saturation, see Fig. 1. In these depositions the N$_2$ purging length for both the reactants was fixed at 6 s based on our preliminary experiments. For the rest of the deposition experiments we employed the following ALD cycle: 2 s Mn$_2$(CO)$_{10}$ / 6 s N$_2$ / 2 s O$_3$ / 6 s N$_2$. 

![Fig. 1](image)

**Fig. 1** Dependence of the GPC value on the precursor pulse lengths. Mn$_2$(CO)$_{10}$ (left) and O$_3$ (right), at the deposition temperature of 80 °C.

Next we investigated the effect of the deposition temperature, varied from 60 to 160 °C, in order to confirm the temperature window for the depositions within which the depositions are well controlled and reproducible. The starting point of 60 °C for our temperature-search experiments was defined by the Mn$_2$(CO)$_{10}$ sublimation temperature of 55 °C, as the deposition temperature cannot be lower than the temperatures of the precursor sources. As can be seen in Fig. 2, the growth rate is ~0.60 Å/cycle at 60 °C, and it increases to ~1.2 Å/cycle when the deposition temperature is 80 °C or higher. The GPC value remains essentially constant up to 120 °C, then increases further being ~1.35 Å/cycle at 140 °C and ~1.5 Å/cycle at 160 °C. We also tested depositions at 200 °C, and for these depositions, the observed GPC value somewhat varied from experiment to experiment. The increase of the growth rate at the higher deposition temperatures could be attributed to the partial decomposition of the manganese precursor. We like to emphasize that the depositions were well-controlled and reproducible at least in the deposition temperature range of 80–160 °C. The general criteria of an ideal ALD-type film growth, i.e. the so-called growth linearity, was tested at 80 °C as is shown in Fig. 2 by varying the number of ALD cycles between 300 and 800: with increasing number of deposition cycles the film thickness increases in an essentially linear manner with no visible nucleation delay in the beginning. Furthermore, when the substrate was exposed to Mn$_2$(CO)$_{10}$ without an oxygen source at 200 °C (400 cycles, 4s pulse length), no Mn was detectable with X-ray fluorescence (XRF) confirming that no CVD type growth by pyrolysis of the precursor occurs within the ALD window.

![Fig. 2](image)

**Fig. 2** (Left) Dependence of the GPC value on the deposition temperature. (Right) Film thickness versus number of ALD cycles for films deposited at 80 °C; the dash line is fitted to the data points, $R^2 = 0.987$.

In Fig. 3, we display GIXRD patterns recorded for our manganese oxide thin films deposited at different temperatures from 80 up to 200 °C. All the films are crystalline. At temperatures between 80–100 °C, our Mn$_2$(CO)$_{10}$+O$_3$ process results in films of the cubic α-Mn$_3$O$_4$ phase. When increasing the deposition temperature to 120 °C or higher the product is Mn$_3$O$_4$ of the tetragonally-distorted spinel structure. For both the phases, increasing the deposition temperature within the respected temperature windows leads to the higher degree of crystallinity. In the case of the Mn$_3$O$_4$ phase, the film deposited at 120 °C shows a sharp peak at 18.0° corresponding to the 101 reflection and weaker peaks at the 2θ angles of 32.4, 36.1, 60.0 and 65.5° assigned to the 103, 211, 224 and 323 reflections, respectively. Then, with increasing deposition temperature new peaks corresponding to the 004, 220 and 321 reflections appear, indicating the enhanced crystallinity of the films. For the α-Mn$_3$O$_4$ phase, the GIXRD pattern of the film deposited at 100 °C shows clear peaks at 23.1, 33.0, 40.7 and 55.2° due to the 211, 222, 411 and 440 reflections.
Since the GIXRD peaks for our low-temperature deposited Mn₂O₃ thin films are relatively broad we sought additional evidence for the trivalent state of manganese in these films from XPS measurements. The Mn 2p and 3s XPS spectra shown in Fig. 4 for the two samples deposited at 80 and 100 °C are fully consistent with trivalent Mn (within the accuracy of the measurement): there is no satellite feature seen between the Mn 2p₁/₂ and Mn 2p₃/₄ peaks in the 2p spectra around 647 eV due to divalent Mn, and in the Mn 3s spectra the splitting of the two multiplet-split components (ca. 5.5 eV) is what one could expect for the trivalent Mn state.²⁴,²⁵ Moreover seen from Fig. 4 is that the spectra for the two samples deposited at 80 and 100 °C are essentially equivalent.

In Table 1, we compare the phase compositions and growth rates realized for our Mn₂(CO)₁₀+O₃ process at different deposition temperatures to those reported in previous literature for the two thermal ALD processes, Mn(thd)₃+O₃ for MnO₂ and Mn(CpEt)₂+H₂O for MnO, and the recently developed PE-ALD processes with ammonia, hydrogen and water plasma. For the thermal Mn(thd)₃+O₃ process for MnO₂, the GPC values achieved are distinctly low (~0.2 Å/cycle).²⁶ With the Mn(CpEt)₂+H₂O process, MnO films have been deposited with the higher rates up to 1.2 Å/cycle.²⁷ For the plasma processes the GPC values achieved are low (~0.2 Å/cycle),²⁸ but the advantage is the possibility to control the oxidation state of manganese by the redox nature of the reactant gases. From Table 1, the GPC values of our Mn₂(CO)₁₀+O₃ process are indeed appreciably high. Moreover, the lowest deposition temperatures of 60–80 °C are essentially lower than those feasible for the previously reported processes. The low deposition temperatures are of particular benefit for potential applications based on temperature-sensitive substrates such as polymers and textiles.²⁶ Most importantly, the low deposition temperatures turned out to be the key for us to be able to deposit the thin films of the metastable Mn₂O₃ phase for the first time by ALD.

We also investigated the effects of post-deposition heat treatments. In particular we wanted to see the phase stability of the Mn₂O₃ phase at elevated temperatures. We thus annealed our Mn₂O₃ films deposited at 100 °C in an oven in air at 400, 500 and 600 °C. As seen from the resultant GIXRD patterns (not shown here) the crystalline phase in the films changed from Mn₂O₃ to Mn₃O₄ upon the annealing, even at the lowest annealing temperature of 400 °C. With increasing annealing temperature, the diffraction peaks due to the Mn₃O₄ phase got sharper, as expected. Hence post-deposition heat treatments may be considered in case the degree of crystallinity of Mn₂O₃ thin films should be further enhanced.

Table 1 Summary of the products and growth rates for different ALD processes for manganese oxide thin films regarding the deposition temperature, from literature and the present work.

<table>
<thead>
<tr>
<th>Dep. temp. (°C)</th>
<th>Product</th>
<th>Precursors and process</th>
<th>GPC (Å/cycle)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>60</td>
<td>MnO₂</td>
<td>Mn₂(CO)₁₀+O₃; Thermal</td>
<td>0.60</td>
<td>present</td>
</tr>
<tr>
<td>80</td>
<td>MnO₂</td>
<td>Mn₂(CO)₁₀+O₃; Thermal</td>
<td>1.16</td>
<td>present</td>
</tr>
<tr>
<td>100</td>
<td>MnO</td>
<td>Mn(thd)₃+H₂O; Thermal</td>
<td>1.2</td>
<td>9</td>
</tr>
<tr>
<td>100</td>
<td>MnO₂</td>
<td>Mn₂(CO)₁₀+O₃; Thermal</td>
<td>1.24</td>
<td>present</td>
</tr>
<tr>
<td>120</td>
<td>MnO₂</td>
<td>Mn₂(CO)₁₀+O₃; Thermal</td>
<td>1.17</td>
<td>present</td>
</tr>
<tr>
<td>140</td>
<td>MnO₂</td>
<td>Mn₂(CO)₁₀+O₃; Thermal</td>
<td>1.35</td>
<td>present</td>
</tr>
<tr>
<td>150</td>
<td>MnO₂</td>
<td>Mn(thd)₃+O₃; Plasma</td>
<td>0.15</td>
<td>18</td>
</tr>
<tr>
<td>150</td>
<td>MnO</td>
<td>Mn(thd)₃+NH₃, Plasma</td>
<td>0.22</td>
<td>18</td>
</tr>
<tr>
<td>160</td>
<td>MnO₂</td>
<td>Mn₂(CO)₁₀+O₃; Thermal</td>
<td>1.52</td>
<td>present</td>
</tr>
<tr>
<td>170</td>
<td>MnO</td>
<td>Mn(thd)₃+H₂O; Thermal</td>
<td>0.84</td>
<td>19</td>
</tr>
<tr>
<td>186</td>
<td>MnO₂</td>
<td>Mn(thd)₃+O₃; Thermal</td>
<td>0.2</td>
<td>6</td>
</tr>
</tbody>
</table>

Fig. 3 GIXRD patterns for our manganese oxide thin films deposited at different temperatures.

Fig. 4 Mn 2p and 3s XPS spectra for two thin-film samples deposited at 80 and 100 °C.
Lastly we discuss the magnetic properties of our spinel-structured Mn$_3$O$_4$ thin films. It is well known that the various manganese oxides display a variety of magnetic properties: MnO is antiferromagnetic, Mn$_3$O$_4$ is ferrimagnetic with a Curie temperature between 39 and 43 K depending on its microstructure and α-Mn$_2$O$_3$ is antiferromagnetic. Fig. 5 shows magnetic hysteresis loops and a magnetic moment versus temperature characteristic for our 35 nm thick Mn$_3$O$_4$ film deposited at 200 °C (the high deposition temperature was selected – though being outside of the ALD window – as it yielded most highly crystalline films). It is apparent that the material is ferrimagnetic as expected. The magnetization per formula unit was calculated using the sample dimensions (3.5 x 14.0 mm$^2$), the film thickness (35 nm), and a density of 4.86 g/cm$^3$ assuming that no other phases than Mn$_3$O$_4$ is present.

The obtained saturation magnetization value of 0.9 µB is lower than most reported values which are typically between 1.4 and 1.85 µB, although values as low as 0.7 µB have been reported for nanostructures. The Curie temperature of 47 K was obtained from a zero-field temperature loop which is compatible with literature values.

**Fig. 5** Magnetic properties of as deposited Mn$_3$O$_4$ thin film grown at 200 °C with thickness of 35 nm: (a) magnetization vs temperature at a field of 10 000 Oe, (b) hysteresis sloops. The diamagnetic contribution was subtracted.

**Experimental**

Thin films of manganese oxides were deposited in an ASM F-120 reactor using Si wafers (p-type 100, Okmetic Ltd.) as substrates. Nitrogen was used as the carrier and purge gas in the depositions. During the deposition, the reactor was kept at a pressure of ca. 2–3 mbar (1.5–2 Torr). Manganese carbonyl was used as the precursor and O$_2$ was used as the oxygen source in the depositions. The sublimation temperature for manganese carbonyl was 55 °C. Depositions were carried out from 60 to 160 °C to investigate the optimal temperature window. At a reaction temperature of 80 °C, the pulse lengths for manganese carbonyl and O$_2$ were varied between 1 and 10 s, and 1 and 8 s, respectively.

The film thicknesses were measured with an X-ray reflectivity (XRR) instrument from PANalytical (X’Pert MPD PRO Alfa 1). Grazing incident X-ray diffraction (GIXRD; X’Pert MPD PRO Alfa 1, PANalytical; Cu-Kα radiation) measurements were carried out to investigate the crystallinity of the samples. The valence of manganese in selected thin-film samples was investigated with x-ray photoelectron spectroscopy (XPS; Kratos Analytical).

The magnetic properties were evaluated using a Quantum Design Dynacool physical property measurement system (PPMS) equipped with a vibrating sample magnetometer (VSM). Magnetic hysteresis loops were measured at temperatures between 10 and 300 K and the magnetization at 10 000 Oe was measured for a temperature interval of 10–400 K.

**Conclusions**

We have developed a new promising ALD process based on the zero-valent manganese precursor complex Mn$_2$(CO)$_{10}$ for the controlled fabrication of crystalline manganese oxide thin films. Ozone is employed as the oxygen source in the process. The process yields homogeneous thin films with an appreciably high growth rate of ca. 1.2 Å per ALD cycle in the low deposition temperature range of 80–160 °C. The low deposition temperature saves energy and allows the use of temperaturesensitive substrates. Most importantly, it enables the growth of manganese oxide thin films with the α-Mn$_2$O$_3$ structure in the lowest temperature region from 80 to 100 °C. This is a novel advantage of our Mn$_2$(CO)$_{10}$+O$_3$ process as there are no ALD processes previously reported for Mn$_2$O$_3$ thin films. Upon increasing the deposition temperature to or above 120 °C, spinel-structured ferrimagnetic Mn$_3$O$_4$ thin films are obtained. The two manganese oxide materials both have interesting future application possibilities which would require/benefit from e.g. thin-film depositions on sensitive/flexible/nano-structured substrates. We foresee that our new low-temperature ALD process enabling the controllable deposition of Mn$_3$O$_4$ and Mn$_2$O$_3$ thin films by adjusting the deposition temperature could be of considerable interest for such applications.

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Notes and references