

Control of Oxygen Nonstoichiometry and Magnetic Property of MnCo_2O_4 Thin Films Grown by Atomic Layer Deposition

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Spinel-structured $(\text{Mn},\text{Co})_3\text{O}_4$ thin films were reproducibly fabricated by atomic layer deposition (ALD) using $\text{Mn}(\text{thd})_3$, $\text{Co}(\text{thd})_2$, and ozone as precursors. A full control of the cation ratio was achieved in the temperature interval 140–160 °C within which also the growth rate remained constant. Precise control of the oxygen content of as-deposited $\text{MnCo}_2\text{O}_{4+\delta}$ films was achieved through postdeposition heat treatments at prefixed temperatures in air and N_2 atmospheres, as evidenced from the monotonous increases of both the unit cell volume and the Curie temperature (T_C) with increasing annealing temperature/decreasing oxygen partial pressure. The T_C value varied from 92 K for the as-deposited $\text{MnCo}_2\text{O}_{4+\delta}$ films to 182 K for the films annealed at 700 °C in N_2 flow.

1. Introduction

The members of the $(\text{Mn},\text{Co})_3\text{O}_4$ spinel system have a variety of applications as materials for catalysts,^{1–5} sensors,⁶ lithium-ion batteries,⁷ and solid oxide fuel cells (SOFCs).^{8–10} Especially the use of MnCo_2O_4 as a protective coating on ferritic stainless steel interconnects in SOFCs has gained increasing interest in recent years. To work efficiently, such a protective layer should be perfectly pinhole-free and uniform. This is where the atomic layer deposition (ALD) technology should appear as a highly promising means to deposit superior-quality $(\text{Mn},\text{Co})_3\text{O}_4$ thin films for protective coatings in SOFCs and other state-of-the-art applications. In an ALD process, the film growth is based on self-limiting surface-controlled reactions achieved through alternate pulsing of the precursors. There are several features that lead to the attractiveness of the ALD method, such as excellent control of thickness and stoichiometry, conformality and uniformity over large area substrates, and very low defect density.¹¹

Yet another interesting aspect of $(\text{Mn},\text{Co})_3\text{O}_4$ spinels is their magnetic properties which have attracted wide attention due to the unusual hysteresis and magnetization process.^{5,12–15} The debate over the actual oxidation states of manganese and cobalt has been going on for decades as research groups have been looking to explain the peculiar hysteresis phenomena and magnetization processes of these spinels.^{12,16–18} Recent publications have been focusing on the effect of the cation ratio on the magnetic behavior of nanocrystalline and thin-film samples, but only few research groups have been interested in the possibility to control the degree of oxygen nonstoichiometry in $(\text{Mn},\text{Co})_3\text{O}_4$ thin films.

Controlling the cation ratio of ternary oxide films by ALD is known to have its challenges,^{19,20} as the film composition is generally found to have a consistent but slightly nonlinear dependency on the ALD precursor pulsing ratio. The control of oxygen stoichiometry in ALD and other thin film samples, however, is clearly a less studied problem. Access to methods for studying the oxygen content of a truly thin film is much more limited compared to bulk materials, where e.g., redox titration is an extremely cost-effective solution. The case of the

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cation-deficient $\text{Mn}_{1-x}\text{Co}_{2-2x}\text{O}_4$ or $\text{MnCo}_2\text{O}_{4+\delta}$ system offers an interesting example of controlling the oxygen stoichiometry of a thin film sample. If prepared at high temperatures, MnCo_2O_4 has a structure of a cation-deficient spinel, but low-temperature synthesis conditions ensure an increased oxygen-to-metal ratio. Earlier studies have shown the effect of the oxygen content on the magnetic characteristics of $\text{MnCo}_2\text{O}_{4+\delta}$ in powder samples.^{12,13} The Curie temperature (T_C) of ferrimagnetic $\text{MnCo}_2\text{O}_{4+\delta}$ has been found to increase remarkably with decreasing oxygen content (or decreasing cation-vacancy concentration). In the present work, not only a novel ALD process is developed to deposit ternary $(\text{Mn},\text{Co})_3\text{O}_4$ thin films but also the possibility to control the oxygen nonstoichiometry in the films have been studied along with the effect of the oxygen content on the magnetic properties. The present study is moreover a valuable addition to the limited number of studies on magnetic properties of oxide materials deposited by ALD.^{21,22}

2. Experimental Section

Thin film depositions of $(\text{Mn},\text{Co})_3\text{O}_4$ with various cation ratios were carried out in a commercial flow-type ALD reactor (F-120 by ASM Microchemistry Ltd.). The alternating precursor pulses were introduced to the reactor chamber using N_2 (>99.999%, Schmidlin UHPN 3000 N_2 generator) as a carrier and purging gas. The metal precursors used, $\text{Mn}(\text{thd})_3$ and $\text{Co}(\text{thd})_2$ (thd = 2,2,6,6-tetramethylheptane-3,5-dionate), were synthesized according to methods described by Hammond et al.²³ and purified by sublimation. Ozone generated from oxygen gas (99.999%) in an ozone generator (Fischer model 502) was used as an oxygen source. The concentration of ozone was $\sim 10\%$ (60 g/cm³) and the gas flow rate during the pulse was about 60 cm³/min (measured for the oxygen gas).

The films were deposited in the temperature range 135–275 °C at a reduced pressure of 2–3 mbar. In this study the manganese and cobalt precursors were evaporated from open glass crucibles held at 116 and 93 °C, respectively. The films were grown on single-crystal substrates of Si(100) without removing the native oxide layer. The silicon substrates of $5 \times 10 \text{ cm}^2$ in size were positioned vertically inside the reaction chamber. The pulsing times of the precursors were chosen sufficiently long in order to obtain complete surface saturation. For all the depositions, a basic ALD cycle consisted of the following pulsing scheme: 2.0 s $\text{Mn}(\text{thd})_3$ or 1.5 s $\text{Co}(\text{thd})_2$ followed by 2.0 s purge, 2.0 s ozone, and 2.0 s purge. After 1000 basic cycles, the typical thickness of a film was about 20 nm. The ALD supercycles were designed to optimize the mixing of the metal components. As an example, the ALD supercycle of a deposition with pulsing ratio $\text{Mn}/\text{Co} = 7:8$ would be comprised of seven alternating basic cycles of Mn and Co and an additional basic cycle of Co. Selected films were annealed after the deposition in a rapid thermal annealing (RTA) furnace PEO 601 (ATV Technologie GmbH). The heat-treatment was performed in air or N_2 gas flow at temperatures ranging from 200 to 900 °C for 10 min.

Grazing incidence X-ray diffraction (GIXRD) measurements were performed on a Panalytical X'Pert Pro MPD Alpha-1 powder diffractometer with $\text{Cu K}\alpha_1$ radiation. The lattice parameters were obtained from profile fitting with the FULLPROF²⁴ software. The thicknesses of the films were measured with X-ray reflectivity (XRR) using the same diffractometer. Representative samples were analyzed by atomic force microscopy (AFM) using a Veeco Dimension 5000 SPM operated in tapping mode with a scan rate of 1 Hz. The actual Mn/Co ratio in the films was routinely determined by an X-ray fluorescence (XRF) spectrometer (Philips PW 1480 WDS) using Rh excitation. The data were analyzed using the UniQuant software which utilizes a DJ Kappa model to calculate simultaneously the composition and the mass thickness of an unknown bulk or thin film sample.²⁵ Compositions of selected films were also analyzed by Rutherford backscattering spectrometry (RBS) using 3 MeV incident He^{2+} ions from a 1.7 MV Pelletron accelerator. Magnetization was measured for the samples with a superconducting quantum interference device (SQUID) magnetometer (Quantum Design, MPMS-XL5) under a magnetic field of 1000 Oe in both field-cooled (FC) and zero-field-cooled (ZFC) modes. The samples for SQUID measurements were prepared by depositing 280 nm of $\text{MnCo}_2\text{O}_{4+\delta}$ on silicon substrates (cut to $4 \times 6 \text{ mm}^2$ pieces) which were then mounted on a straw with the film surface perpendicular to the direction of the applied magnetic field. The measurement temperature was from 5 to 300 K.

3. Results and Discussion

The $(\text{Mn},\text{Co})_3\text{O}_4$ film growth rate was studied in the temperature range from 135 to 275 °C. A temperature window for ALD-type growth, i.e., the temperature range where the growth rate remains essentially constant (here $\sim 0.2 \text{ Å/cycle}$), was observed at 140–160 °C. The ALD window observed for $(\text{Mn},\text{Co})_3\text{O}_4$ is very narrow considering the corresponding temperature windows of the binary processes for Co_3O_4 and MnO_x with ALD-type growth in the temperature ranges 114–307 °C^{26,27} and 138–210 °C,²⁸ respectively. The lower limit of 140 °C for $(\text{Mn},\text{Co})_3\text{O}_4$ is certainly explained by the lower limit of the growth of MnO_x ; then, however, above 160 °C the film quality deteriorated drastically resulting in films with serious thickness variations. Moreover it was revealed that at higher temperatures the growth rate of the films increased rapidly with increasing temperature. In Figure 1, the growth rate and the Mn content are plotted for approximately 40 nm thick $(\text{Mn},\text{Co})_3\text{O}_4$ films grown with a cation pulsing ratio of $\text{Mn}/\text{Co} = 1:1$. At 175 °C, the growth rate is already 2.5 times higher than within the ALD window, and above 200 °C even 7 times greater growth rates were observed (not shown in Figure 1) indicating a complete lack of control of the film growth. Such drastic changes were not observed in the Mn/Co ratio with increasing temperature, see Figure 1. The Mn

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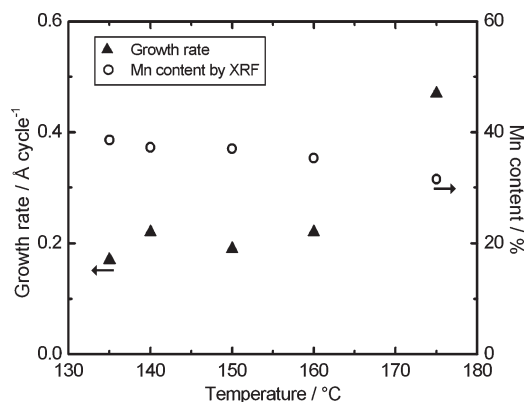


Figure 1. Temperature dependences of the growth rate and the Mn content (against the total metal content) for $(\text{Mn},\text{Co})_3\text{O}_4$ films deposited with a Mn/Co pulsing ratio of 1:1 (the number of basic ALD cycles was 2000).

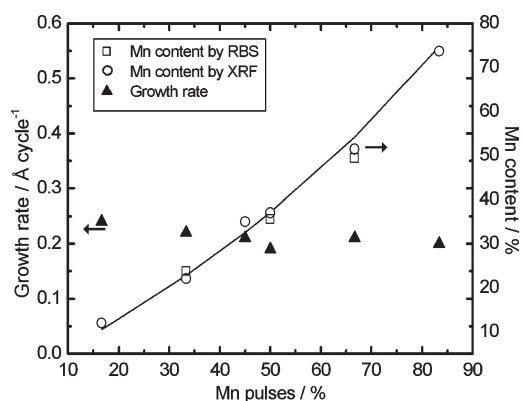


Figure 2. Effect of the pulsing fraction of $\text{Mn}(\text{thd})_3$ on the Mn content (by XRF and RBS) and the growth rate of $(\text{Mn},\text{Co})_3\text{O}_4$ films at deposition temperature 150°C (the thickness of the films was 35–50 nm). The sizes of the symbols correspond to estimated errors. The fitted curve is calculated using eq 1 and the coefficients $U_{\text{Co}} = 1$ and $U_{\text{Mn}} = 0.59$.

content of the films decreases slightly with increasing temperature, but the observed trend is very subtle. In the temperature range $175\text{--}230^\circ\text{C}$, no further decrease was observed in the Mn content. However, at 275°C the observed Mn content was suddenly increased moreover showing rather poor reproducibility. Between 140 and 160°C , the Mn content is only slightly lessened, thus verifying the easily controlled ALD-type growth in this temperature window. As expected, the films were rather smooth both before and after the postdeposition heat treatment. The AFM analysis showed root-mean-square (rms) roughnesses of 1.12 and 1.97 nm for as-deposited films grown with Mn/Co pulsing ratios of 1:5 and 5:1, respectively. Films deposited with a Mn/Co pulsing ratio of 1:1 showed a rms roughness of 1.99 nm after annealing at 800°C in air.

For a more thorough investigation of the process, the effect of the Mn/Co pulsing ratio on the composition and the deposition rate of $(\text{Mn},\text{Co})_3\text{O}_4$ films deposited at 150°C is illustrated in Figure 2. According to both XRF and RBS analysis, the dependency of the measured Mn/Co ratio on the pulsing ratio is nearly linear. The cation stoichiometry was therefore easily controlled by a simple adjustment of the pulsing ratio. Furthermore, the film quality and the cation stoichiometry were maintained

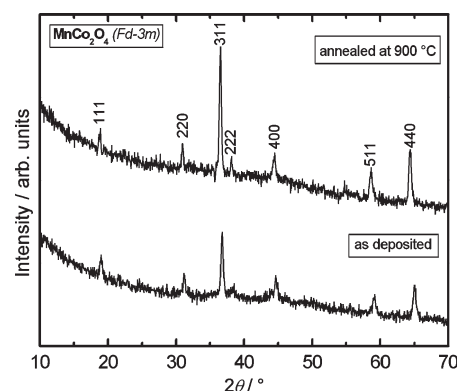


Figure 3. XRD patterns for as-deposited and postdeposition annealed (in air at 900°C) $\text{MnCo}_2\text{O}_{4+\delta}$ films. The indices are for the cubic space group $Fd\bar{3}m$.

while depositing even much thicker films, i.e., 280 nm, indicating an exclusively surface-reaction controlled ALD process. As seen in Figure 2, the deposition of cobalt is slightly amplified in comparison to manganese. According to Ylilammi²⁹ and Lie et al.,²² a very natural explanation would be the adsorption of $\text{Co}(\text{thd})_2$ precursor molecules as $\text{Co}(\text{thd})$ while $\text{Mn}(\text{thd})_3$ is most likely adsorbed as $\text{Mn}(\text{thd})_2$. The concept of surface coverage by different precursors introduced by Nilsen et al.¹⁹ leads to eq 1 for the Mn–Co-system, where U_x , D_x and P_x represent the surface utilization coefficient, the deposited stoichiometry, and the pulsed stoichiometry of component x , respectively. When U_{Co} was set to 1 and the experimental data in Figure 2 were fitted to eq 1, the value of $U_{\text{Mn}} = 0.59$ was obtained.

$$\frac{D_{\text{Mn}}}{D_{\text{Mn}} + 1 - D_{\text{Co}}} = \frac{P_{\text{Mn}} U_{\text{Mn}}}{P_{\text{Mn}} U_{\text{Mn}} + P_{\text{Co}} U_{\text{Co}}} \quad (1)$$

For our final experiments we fixed the Mn/Co pulsing ratio to 7:8 in order to correspond to the targeted spinel phase of $\text{MnCo}_2\text{O}_{4+\delta}$. Composition analysis (by XRF) confirmed the actual Mn/Co ratio to be 1:2.00(5). X-ray diffraction data for as-deposited $\text{MnCo}_2\text{O}_{4+\delta}$ films grown in the temperature range $140\text{--}275^\circ\text{C}$ showed weak reflections of the expected spinel structure without a trace of binary oxide impurities as seen in Figure 3. Postdeposition annealing improved the crystal quality of the films, and it was clearly verified that all the diffraction peaks could be indexed in the cubic cell for spinel compounds with space group $Fd\bar{3}m$. For the annealed films, a gradual increase in the lattice parameter a was detected with increasing annealing temperature (Figure 4) from 8.11 Å for the as-deposited films to 8.26 Å for films annealed at 800°C in N_2 gas flow. The observed magnitude of lattice contraction well agrees with data reported for bulk $\text{MnCo}_2\text{O}_{4+\delta}$ samples.¹² The increase in lattice parameter a and accordingly in unit cell volume reflects the decrease in oxygen content (or in the oxygen to metal content ratio).^{12,15} Loss of the excessive oxygen from the spinel structure of MnCo_2O_4 results in the

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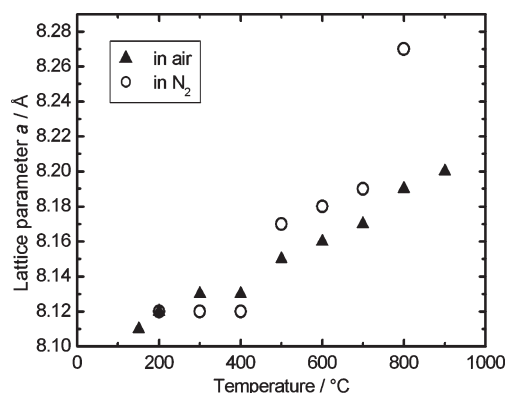


Figure 4. Increase in the lattice parameter a with increasing postdeposition annealing temperature for the $\text{MnCo}_2\text{O}_{4+\delta}$ films. The triangles indicate the values for the films annealed in air, and the circles show the values for the films annealed in N_2 gas flow.

progressive reduction of manganese (Mn^{IV} to Mn^{III}) and/or cobalt (Co^{III} to Co^{II}).^{12,16–18} From Figure 4, compared to annealing in N_2 , the increase in the unit cell volume and hence the degree of reduction is somewhat less pronounced when the heat treatment is performed in air. Here we should also mention that annealing in N_2 at 900 °C decomposed the spinel structure, while air-annealing at the same temperature did not result in any noticeable changes in sample quality.

The information on the oxygen nonstoichiometry of $\text{MnCo}_2\text{O}_{4+\delta}$ is vital when it comes to understanding the magnetic properties of these spinels as the magnetic characteristics of $\text{MnCo}_2\text{O}_{4+\delta}$ are strongly dependent on the oxidation states of manganese and cobalt. Thus, it is clear that while studying the magnetic properties of such compounds the possibility for alterations in oxygen stoichiometry should always be acknowledged. Although the precursor chemistry implies oxidation states +III for manganese and +II for cobalt, the fact that the spinel structure allows changes in its oxygen content and moreover the presence of such a strong oxidizer as ozone, very few assumptions can be made on the oxygen content of the as-deposited films. This is the case especially when ALD is employed as a deposition method due to the exceptionally low deposition temperature.

In order to study the effect of the postdeposition annealing conditions, and thus, the changing oxygen content on the magnetic properties of $\text{MnCo}_2\text{O}_{4+\delta}$ films, the temperature dependence of magnetic susceptibility χ was measured for various $\text{MnCo}_2\text{O}_{4+\delta}$ thin film samples with measured Mn/Co ratio = 1:2. Figure 5 displays the data for two representative samples, a film annealed at 500 °C in air and a film annealed at 700 °C in N_2 gas flow. As expected, the T_C value of the ferrimagnetic $\text{MnCo}_2\text{O}_{4+\delta}$ was affected by the conditions of the postdeposition heat treatment. The magnetic measurements revealed an increasing trend in T_C with decreasing a parameter (see the inset of Figure 5),

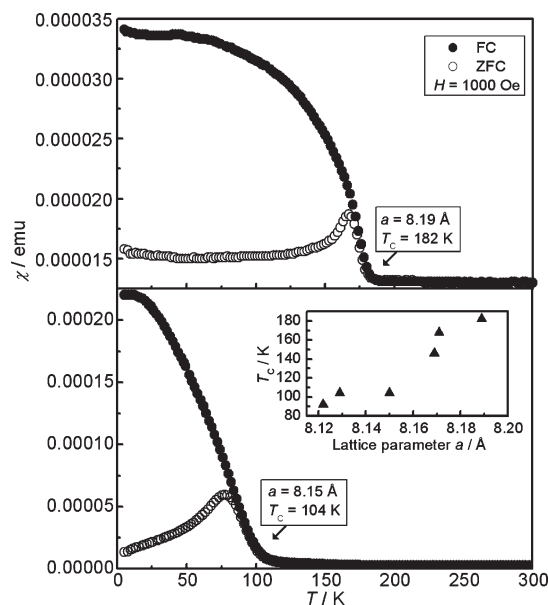


Figure 5. Temperature (T) dependence of magnetic susceptibility (χ) for $\text{MnCo}_2\text{O}_{4+\delta}$ thin films annealed at 500 °C in air (lower panel) and at 700 °C in N_2 gas flow (upper panel). The inset shows the variation of the Curie temperature of $\text{MnCo}_2\text{O}_{4+\delta}$ with the lattice parameter a .

confirming that the oxygen stoichiometry indeed had been successfully controlled in our spinel-structured $\text{MnCo}_2\text{O}_{4+\delta}$ thin films through the postdeposition heat treatments.

4. Conclusions

High-quality partially crystalline $(\text{Mn},\text{Co})_3\text{O}_4$ thin films were produced with the ALD technique at relatively low deposition temperatures. Reproducible ALD-type growth was achieved in a temperature interval 140–160 °C. Because of excellent control of cation stoichiometry, the deposition of films with the targeted MnCo_2O_4 stoichiometry was rather straightforward. The concept of precursor surface area coverage was moreover found to apply well with the experimental results with $U_{\text{Mn}} = 0.59$ and $U_{\text{Co}} = 1$. Although X-ray reflections of the expected spinel (cubic, $Fd\bar{3}m$) structure were already observed for the as-deposited films, postdeposition heat treatment was needed to enhance the crystal quality of the films. The conditions of the postdeposition heat treatment were found to affect not only the lattice parameter a but also the Curie temperature of the ferrimagnetic $\text{MnCo}_2\text{O}_{4+\delta}$ phase. Magnetic measurements revealed an increase in the T_C value with increasing postdeposition annealing temperature/decreasing oxygen partial pressure confirming the continuous loss of oxygen from the spinel structure upon annealing up to 900 °C.

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