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Thin film deposition of lanthanum manganite perovskite by the ALE process

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Deposition of thin films of $LaMnO_3$ from β-diketonate-type (thd) precursors and ozone in an ALE reactor has been demonstrated. At low temperatures, the Mn–O growth from the $Mn(thd)_3$ precursor is retarded by the growth of the La–O deposit. By tuning of the pulsing ratio, full control of the stoichiometry of the deposited film is achieved in the temperature interval 300–400 °C. In this temperature range, the composition set by the pulsing ratio is transferred, within a few percent accuracy, to the deposited thin film. Indications for an 'ALE window' are found around 250–300 °C. Amorphous $LaMnO_3$ films could be deposited at temperatures as low as 250 °C, however, the deposition of crystalline films requires temperatures above 350 °C. X-Ray diffraction analyses show that the crystalline $LaMnO_3$ film was of the rhombohedral type with $a = 5.46(2)$ Å and $\alpha = 60.28(10)°$.

Introduction

Materials with the ABO_3 perovskite-type structure exhibit a vast range of electric and magnetic properties dependent on the elements (A,B) as well as the exact composition. This class of materials therefore provides potential components for electric and magnetic devices. Their properties are often controlled and monitored by variation in the oxygen stoichiometry or by substitution on the A and/or B sites. In recent years there has been a marked increase in research on thin film processing, motivated by the fact that several advanced applications require material in thin film form. This also applies to research on thin oxide films, where materials with the perovskite-type structure are well represented. The growth of the same thin film material has typically been attempted by a variety of methods. One motivation for this is that different methods often produce materials with different microstructures, which in turn can affect their properties.[1–5]

The present work focuses on the growth of thin films of the $LaMnO_{3+\delta}$ perovskite-type oxide *via* the atomic layer epitaxy (ALE) method. Owing to its intriguing physical properties and potential applications, $LaMnO_3$ and its solid-solution derivatives have received considerable attention. For instance, materials with partial substitution of La by divalent cations (Ca, Ba, Sr, Pb, Cd) or with vacancies introduced at the La sites show colossal magnetoresistance (CMR) properties,[6–8] whereas $(La,Sr)MnO_3$ materials are commonly used in solid oxide fuel cell (SOFC) prototypes working at high temperatures[9] and are also of interest as oxygen sensors.[10] The CMR effect is believed to result from a mixed valence situation with the presence of both Mn^{III} and Mn^{IV} species.[11] Thin films of $La_{1-x}A_xMnO_3$ (A = Ca, Ba, Sr, Pb) are reported to give larger CMR values than bulk samples. There is also interest in exploiting their catalytic activity for combustion of gases like CO and NO_x as well as for volatile organic compounds (VOC).[12–14]

Thin films of $(A,La)MnO_3$ (A = Ca, Sr, Ba, Pb) have previously been deposited by methods such as pulsed laser deposition (PLD),[3–5,15–17] facing-target sputtering,[18] RF sputtering,[19,20] ion beam sputtering,[21] molecular beam epitaxy (MBE),[22,23] chemical vapour deposition (CVD)[24] and its metalorganic variant (MOCVD),[25,26] spray pyrolysis,[27] spin coating with sol–gel epitaxial growth,[28] metalorganic deposition from solution[29] and electrodeposition.[30] Among these, PLD is the most frequently used method and it allows control over the stoichiometry up to a certain level. All these methods, except for spin coating, (MO)CVD and electrodeposition, are so-called 'line of sight' methods where a uniform coating cannot be expected. Furthermore, most of them require either post-annealing or deposition at a rather high temperature in order to arrive at a crystalline film.

Only a few ternary oxides have so far been grown with the ALE technique.[31,32] However, its potential for growing thin films of perovskite-type oxides has been demonstrated for $LaNiO_3$ and $LaCoO_3$[33,34] and more recently for $SrTiO_3$.[35] The ALE method is attractive since it can provide excellent control of thickness, stoichiometry, step coverage and uniformity over large area substrates. Furthermore, a crystalline film can often be achieved at lower temperatures than with other techniques.[36] This would be important if one considers applications such as integrated circuit units.

Experimental

Thin films were grown in a flow-type ALE reactor which has been described elsewhere.[37] Freshly synthesised $La(thd)_3$ and $Mn(thd)_3$ (thd = 2,2,6,6-tetramethylheptane-3,5-dionate) were used as precursors and ozone as the oxidiser. The stability and volatility of the precursors were checked by TG under simulated ALE conditions (reduced pressure of 1–2 mbar). Ozone was produced by feeding oxygen gas (99.999%) into the reactor through an ozone generator (Fischer model 502). The reactant pulses were separated by nitrogen gas (99.999%) purging. The pulsing period for the lanthanum and manganese precursors was 1.8 s, whereas the N_2 purging period was 2.5 s. Ozone was pulsed for 1 s followed by N_2 purging for 3 s. The purging and pulsing times were chosen on the basis of earlier ALE studies on $LaNiO_3$ and $LaCoO_3$[33,34] and these parameters are not the subject of more detailed study here. However, a few tests were performed with variation of the pulsing and purging times without observing any notable difference. For the deposition of films with varying composition and thickness, the pulsing sequences were chosen to maximise the probability of proper mixing of the components, *i.e.* first $La(thd)_3$, then O_3, followed by $Mn(thd)_3$ and finally O_3 again.

The films were grown on Si(100), soda lime and aluminium foil substrates under a pressure of 1 mbar. Altogether six

50 × 50 mm^2 substrates were vertically accommodated in a back-to-back configuration (see Fig. 1). Substrate **1** and **2** (left hand side) were of silicon, **1** and **2** (right hand side) were of soda lime and for substrate **3** both sides were of aluminium foil. Depositions were made in the temperature interval 200–400 °C. Film growth was studied as a function of deposition temperature and of pulsing ratio. The films were characterised in the as-deposited state.

As a preliminary test, films of MnO_x were grown with $Mn(thd)_3$. The growth was found to proceed in a manner similar to that described for $Ni(thd)_3$ and $Co(thd)_3$.[33,34] However, a major difference stems from the fact that Mn shows a larger variation in oxidation states than Ni and Co. As a consequence, a variety of manganese oxide phases were formed: MnO_2 at 180 and 200 °C, Mn_2O_3 at 250 °C and Mn_3O_4 at 350 °C.

Characterisation

Phase identification was performed by X-ray diffraction (XRD) measurements with a Philips MPD 1880 powder diffractometer using Cu-Kα radiation. La and Mn concentrations were determined using a Philips PW 1480 X-ray fluorescence spectrometer equipped with a Cr X-ray tube. La Lα was measured with 40 kV, 60 mA and a LiF(220) analysing crystal. For Mn Kα, settings of 60 kV, 40 mA and a Ge(111) analysing crystal were used. A self-supporting $LaMnO_3$ pressed powder sample served as a standard for defining instrumental sensitivity factors corresponding to the analytical lines. Subsequent data analysis was performed with UNIQUANT 2.5 software based on fundamental parameters. UNIQUANT utilises the DJ Kappa model to calculate simultaneously the composition and mass thickness of an unknown bulk or thin film sample.[38] Since oxygen could not be quantified with the present spectrometer set-up, it was assumed that there were 1.5 oxygen atoms for each La and Mn atom in the thin film layer. Furthermore, the growth rate was evaluated, when possible, by fitting of transmittance curves[39] recorded with a Hitachi U-2000 double-beam spectrophotometer in the region 370–1100 nm. However, only the thinner films were sufficiently transparent to be evaluated spectrophotometrically.

Results and discussion

A major motivation for this work was to demonstrate the feasibility of growing multi-element films with controlled stoichiometry in an ALE reactor. Hence, the work was focused on growing films at different deposition temperatures and by variation of the pulsing ratio of the precursors.

The thin films were deposited from $La(thd)_3$ and $Mn(thd)_3$ precursor batches heated in separate furnaces. By varying the source temperature, the optimum sublimation temperature was found to be 115 °C for $Mn(thd)_3$ and 175 °C for $La(thd)_3$. After completion of deposition, neither of the source crucibles showed any residue which could indicate a partial decomposition of the precursors. The precursors are hence considered to be relatively stable, in accordance with the TG data and our earlier experiences.[33,34]

The deposition temperature showed a significant influence on the growth rate of the thin films, see Fig. 2. Thickness measurements were made for both the first and the second substrate in the flow direction. The thickness was measured as an average over a 450 mm^2 circular area in the middle of the substrate, *i.e.* over an area which in all cases was considered uniform.

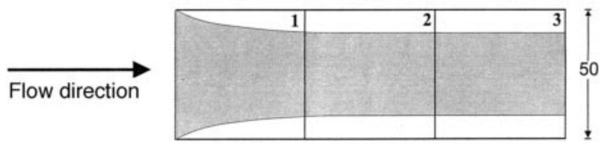

Fig. 1 Substrate arrangement with respect to the direction of the gas flow. Dimensions in mm.

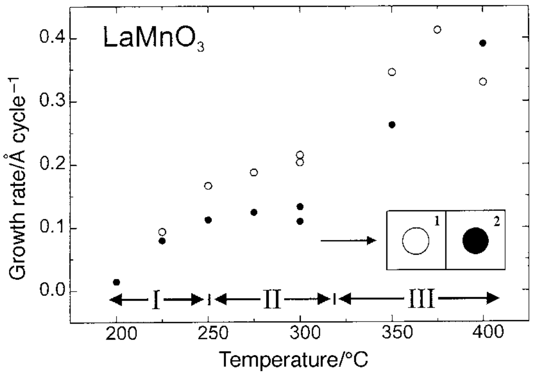

Fig. 2 Growth rate as a function of temperature for substrates **1** and **2**. Open and filled symbols refer to substrate positions.

The temperature dependence of the growth rate indicates that at least three different growth mechanisms are operative. For the range 200–250 °C, the rate increases steadily with temperature. It is believed that deposition is kinetically hindered in this range and that only a small amount of the precursor has sufficient energy to bond chemically to the surface.

In the temperature region 250–300 °C, there is no significant variation in the growth rate with the deposition temperature. This region, marked II in Fig. 2, appears to represent an 'ALE window'[40] since the growth is surface controlled and only affected by the temperature to a small extent.

The small variation of growth rate that is nevertheless observed in the 'ALE window' could indicate rearrangement of the surface species at different temperatures. It is indeed possible that the growth rate is influenced by the packing of the bulky La and Mn precursors on the surface.

For temperatures above *ca.* 250 °C, substrate **1** shows a systematically slightly larger growth rate than the succeeding substrate, Fig. 2. This may be caused by several effects: (i) full surface saturation cannot be achieved within the length of the pulsing cycles chosen, (ii) CVD-type growth may take place for substrate **1** and/or (iii) the concentration gradient in the flow direction is due to the fact that thd ligands released at an early stage will deposit on later parts and this will partially prevent the subsequent adsorption of the precursors.

The ALE system was tested for possible gas leakage of the thd precursors which could lead to CVD-type growth. However, on pulsing of the ozone reactant only, no film was obtained and CVD-type growth could therefore be excluded. In the growth of manganese oxide films, only a slight thickness variation was observed when the length of the Mn pulses was varied. A few tests were carried out to study the effect of the pulsing cycles on the growth of $LaMnO_3$ films, but no large variation was found either.

A third growth mechanism is indicated at temperatures between 300 and 400 °C (region III of Fig. 2). The growth rate in this interval increases with temperature. This is believed to reflect a partial decomposition of the precursors (the thd compound may lose one or two of its three ligands)[41] which makes it possible that a larger amount of the precursor can chemically bond to the surface in one cycle.

The obtained films are not uniform in all directions and exhibit a rather sharp decrease in thickness towards the edges that were parallel to the flow direction (see Fig. 1). This type of gradient was also found with pure $Mn(thd)_3$, $Ni(thd)_3$ and $Co(thd)_3$ precursors[33,34] and is therefore believed to be related to reactor gas flow characteristics or to reactions between these precursors, the substrate and ozone.

The choice of deposition temperature has a pronounced effect on the stoichiometry of the film. Fig. 3 shows how the Mn content of the obtained films varies with deposition temperature for fixed 1 : 1 (La : Mn) pulses. The films become poor in Mn content at temperatures below 250 °C. The film deposited at 200 °C consists almost entirely of lanthanum oxide and the growth rate is very low. However, at the same temperature it is possible to grow oriented MnO_2 films at a growth rate of at least 0.2 Å per cycle by pulsing $Mn(thd)_3$ and ozone. This shows that presence of La–O retards the growth of Mn–O at lower temperatures. The retarding effect on Mn–O growth may possibly be caused by unfavourable surface sites for $Mn(thd)_3$ to adsorb at. However, this hypothesis requires further investigation.

In order to achieve control of the La : Mn stoichiometry of the film, depositions were performed at 300 and 400 °C with varying pulsing ratios. The resulting Mn content is shown in Fig. 4. It appears possible to control the La : Mn stoichiometry of the film within a few percent by adjusting the pulsing ratio. It can be seen that the films grown at 400 °C on substrate **2** show consistently higher Mn contents than those on substrate **1**, in particular at higher Mn pulsing ratios. The films grown on substrate **1** at 300 °C show a slight decrease in their Mn contents as the La : Mn ratio increases. This may indicate that La–O is retarding the growth of Mn–O, even at this temperature.

XRD measurements were conducted on films grown on Si(100) substrates (in position **2**). The observed diffraction profiles of some samples from selected deposition conditions are shown in Fig. 5. The data indicate that it is possible to grow reasonably crystalline films at a temperature as low as 350 °C. The degree of crystallinity, as judged from the FWHM of the peaks, improves with increasing deposition temperature as expected. The XRD patterns fit well with that of $LaMnO_3$ and show that the films are polycrystalline with a rhombohedral type structure, $a = 5.46(2)$ Å and $\alpha = 60.28(10)°$, being thus quite similar to powder samples.

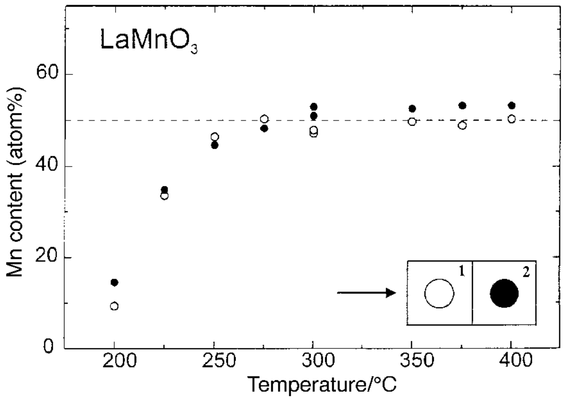

Fig. 3 Measured Mn content (in atom% of cation constituents) for attempted growth of $LaMnO_3$ thin films as a function of temperature. Open and filled symbols refer to substrate positions.

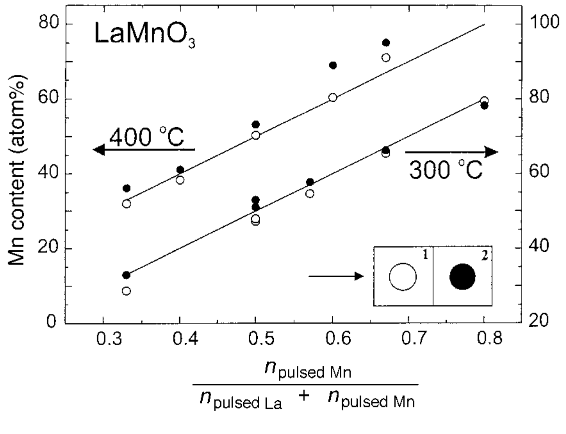

Fig. 4 Measured Mn content (in atom% of the cation constituents) *versus* the pulsing fraction of Mn precursor at reactor temperatures of 300 and 400 °C. Lines represent the theoretical situation. Open and filled symbols refer to substrate positions.

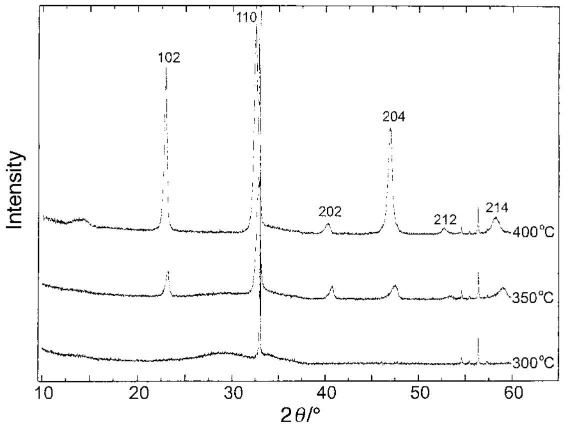

Fig. 5 XRD patterns recorded for films deposited on Si(100) in substrate position **2** at different deposition temperatures. Miller indices of a rhombohedral cell in a hexagonal setting are given on the upper diffractogram. Unmarked peaks are from partially oxidised Si substrate.

Conclusion

Thin film growth of $LaMnO_3$ in an ALE reactor has been demonstrated from β-diketonate-type precursors and ozone. It was shown that La–O retards the growth of Mn–O from $Mn(thd)_3$ at low temperature. Film growth with a good control of stoichiometry has been demonstrated at temperatures between 300 and 400 °C. At these temperatures the stoichiometry of the pulsing ratio is transferred, within a few percent accuracy, to the thin film. $LaMnO_3$ can be deposited at temperatures as low as 250 °C, but crystalline films can be achieved at temperatures above 350 °C.

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