Deposition of $LaNiO_3$ thin films in an atomic layer epitaxy reactor

Helene Seim,[a]† Heini Mölsä,[a] Minna Nieminen,[a] Helmer Fjellvåg*[b] and Lauri Niinistö[a]

[a]*Helsinki University of Technology, Laboratory of Inorganic and Analytical Chemistry, FIN-02150 Espoo, Finland*
[b]*University of Oslo, Department of Chemistry, P.O. Box 1033 Blindern, N-0315 Oslo, Norway*

$LaNiO_3$ thin films have been deposited in an atomic layer epitaxy (ALE) reactor, using $La(thd)_3$, $Ni(thd)_2$ and ozone as reactants, thereby proving the feasibility of the ALE technique to produce films of ternary oxides. Depositions were made on Corning glass in the temperature range 150–450 °C. The growth conditions were studied and the growth rate showed a linear dependence on the number of cycles. At 400 °C the growth rate was 0.24–0.26 Å per cycle. The growth rate of the $LaNiO_3$ thin films was greatly influenced by the deposition temperature but in the temperature range 215–250 °C the growth saturated at 0.08 Å $cycle^{-1}$ independent of the deposition temperature, thus indicating an ALE window. As-deposited thin films were amorphous but crystallized when heated at 600 °C. Simultaneously the colour of the films changed from yellow–brown to black. Possible reasons for the colour changes are discussed. Resistivity measurements showed that the crystalline thin films were metallic, $\rho = (5\text{–}20) \times 10^{-6}\ \Omega$ m. The amorphous thin films had resistivity values five orders of magnitude larger, $\rho > 3\ \Omega$ m. According to scanning electron microscopy (SEM) and atomic force microscopy (AFM), the films were homogeneous and dense. The surface roughness increased on crystallisation. X-Ray photoelectron spectroscopy (XPS) and magnetic susceptibility measurements were employed in order to further characterize the amorphous and crystalline thin films.

Perovskite-type related oxides have found a variety of applications such as ferroelectrics, sensors, superconductors, electrodes and catalysts.[1,2] Some of these oxides, *e.g.* $PbTiO_3$ and $LaNiO_3$, are simple compounds from a chemical point of view, whereas the related high-temperature superconducting materials have a very complex chemistry with three or more different cations in the unit cell. Our interest is mainly focused on $LaNiO_3$, which is metallic, exhibits Pauli paramagnetic behaviour and has a slightly rhombohedrally distorted perovskite-type structure. The metallic conductivity of $LaNiO_3$ makes the material interesting for electrode applications.[3,4] Quite often, metallic conductivity is first achieved for related oxides when turning to aliovalently substituted systems, such as *e.g.* $La_{1-t}Sr_tMnO_3$[5] and $La_{1-t}Ca_tCrO_3$,[6] where the chemical complexity is larger.

The metallic properties and a good lattice match with other perovskite-type oxides like $PbTiO_3$ and $YBa_2Cu_3O_{7-\delta}$ (YBCO), make $LaNiO_3$ a very interesting candidate for thin film applications. Thin film depositions of $LaNiO_3$ have been reported by various techniques including laser deposition, spray combustion flame technique, rf magnetron sputtering, spray-ICP and spin coating followed by pyrolysis[7–13] where the motivation has been the use of $LaNiO_3$ as an electrode, as a substrate for YBCO or as the metallic part in SNS junctions. The crystal structure of the thin films of $LaNiO_3$ is reported to be close to cubic,[9–11] possibly corresponding to a high-temperature modification of $LaNiO_3$, which is reported to exist above 940 °C.[14] This temperature is, however, above the thermal decomposition limit.[15] Recent studies indicate that the cubic modification occurs for stoichiometric samples and that slight deviations in the oxygen content or the incorporation of alkali-metal impurities give a rhombohedral distortion.[16]

In the case of laser deposition[7,8] $LaNiO_3$ was grown on $LaAlO_3$, $SrTiO_3$ and yttrium-stabilised zirconia (YSZ) substrates. Depositions were carried out at substrate temperatures between 440 and 700 °C under an oxygen partial pressure of $(1.6\text{–}4.0) \times 10^{-4}$ bar. The method was successful in providing films with low resistivity, *ca.* $1.5 \times 10^{-6}\ \Omega$ m at 15 K. The films obtained at 500 °C showed expected Pauli paramagnetic properties, whereas those obtained at 700 °C showed a larger Curie–Weiss contribution to the magnetic susceptibility, thereby indicating the presence of local moments, probably Ni^{II} species.[8]

In the spray-ICP technique at atmospheric pressure, the $LaNiO_3$ films were deposited on MgO, sintered high-purity alumina, Si or sapphire substrates at temperatures between 350 and 800 °C.[9] (111)- and (100)-oriented $LaNiO_3$ films were obtained on sapphire (001) and MgO (100) substrates,[9] respectively. The resistivity of films deposited above 600 °C was found to be *ca.* $4 \times 10^{-6}\ \Omega$ m. $LaNiO_3$ synthesized during such experiments was found to have better characteristics as the bottom electrode for $PbTiO_3$ ferroelectric films than the conventional Pt electrodes.

Multilayer thin films of $BaTiO_3$–$LaNiO_3$ and $PbTiO_3$–$LaNiO_3$ have been deposited on MgO substrates by using the spray combustion flame technique.[10] In similar studies $LaNiO_3$ was deposited on sintered alumina, sapphire and MgO.[11] The lowest resistivity, $6 \times 10^{-6}\ \Omega$ m, was measured on a $LaNiO_3$ film deposited on MgO at a temperature above 700 °C.

As a bulk material, $LaNiO_3$ can be synthesized in a rather straightforward way, provided that care is taken to avoid decomposition owing to the reduction of Ni^{III} at high temperatures (above 800 °C in pure oxygen) and/or under low oxygen partial pressures. Decomposition will give phase mixtures consisting of $La_2Ni_2O_5$, $La_4Ni_3O_{10}$, La_2NiO_4, $LaNiO_2$, NiO, La_2O_3 and Ni depending on the conditions.[14–16] The synthesis is best performed by using sol–gel precursors, *e.g.* citrate gels,

---

† Present address: University of Oslo, Department of Chemistry, P.O. Box 1033 Blindern, N-0315 Oslo, Norway.

or in basic carbonate melts. At low temperatures where structural reconstructions are kinetically hindered, $LaNiO_3$ can be reduced continuously in a topotactic reduction from $LaNiO_3$ to $LaNiO_{2.5} = La_2Ni_2O_5$.[17] The latter type of reduction can usually be performed for perovskite-type oxides with transition-metal cations in high oxidation states. During the reductions, the properties of the materials may change dramatically, *e.g.* the conductivity may be changed by several orders of magnitude. Hence, tuning the physical properties of the bulk and presumably also thin films is partly possible *via* monitoring the oxygen content of the material during thermal treatment.

The motivation for pursuing thin film deposition of $LaNiO_3$ is manifold. Besides the applicational aspects of $LaNiO_3$, it is of fundamental interest prior to further studies of perovskite-type oxide thin films to demonstrate the feasibility of CVD and ALE techniques for producing $LaNiO_3$ thin films. Thin film growth of binary metal oxides by ALE has been demonstrated for several compounds but the more complex ternary compounds have not yet been studied.[18] The chemical complexity of $LaNiO_3$ is fortunately considerably smaller than that encountered, for example, in materials like $La_{1-t}Sr_tMnO_3$ and $YBa_2Cu_3O_{7-\delta}$. Secondly, it is of interest to produce a $LaNiO_3$ thin film for which the physical properties subsequently can be adjusted by subjecting it to temperature/oxygen partial pressure conditions which are selected independently on the basis of studies of bulk samples.

Experimental

Film growth

Films were grown in a flow-type ALE reactor which has been described elsewhere.[19] $La(thd)_3$ and $Ni(thd)_2$ (thd = 2,2,6,6-tetramethylheptane-3,5-dionate), synthesized in Espoo, were used as precursors and ozone as the oxidizer. Ozone was produced by feeding oxygen gas into the reactor through an ozone generator (Fischer model 502). The concentration of ozone was *ca.* 10% (60 g m^{-3}). The gas flow-rate during the pulse was *ca.* 60 cm^3 min^{-1}, measured for the oxygen gas. The reactant pulses were separated by nitrogen gas purging. After lanthanum and nickel pulses the purging time was 2.5 s and after ozone it was 3 s. Typical reactant pulse durations were 1.8 s for $La(thd)_3$ and $Ni(thd)_2$ and 1.0 s for ozone. Pulsing sequences used for obtaining various thin film thicknesses were chosen as a multiplet of a basic cycle consisting of 15 alternating cycles of La and O precursors followed by 15 cycles of Ni and O precursors.

The films were grown on Corning 7059 glass substrates under a pressure of 0.4–1 mbar (measured before the reaction chamber). The substrate size used was *ca.* 5×5 cm^2. Depositions were made in the temperature range 150–500 °C. The growth rate was studied, both as function of temperature and by varying the number of cycles $(30–272) \times 30$ at a selected temperature, 400 °C.

Several films were subsequently heated in a tube furnace in flowing oxygen at 600 °C for 12 h. Other thin films were heat-treated in a tube furnace which was connected to a gas mixing system and an oxygen sensor (yttrium-stabilised zirconia, Dansensor). Reduced oxygen partial pressure was obtained by using N_2 $[p(O_2) \approx 3.8 \times 10^{-4}$ bar] or a CO_2–Ar mixture with 2% H_2 $[p(O_2) \approx 10^{-24}$ bar].

Characterization

Crystal structure data and crystallite orientation of the films were determined by X-ray diffraction (XRD) measurements with a Philips MPD 1880 powder diffractometer using Cu-Kα radiation. The average thickness of a deposited thin film was estimated by measuring the thickness at three different points using a profilometer (Veeco Instruments Dektak 3030). The steps were etched by 5 mol dm^{-3} hydrochloric acid. A four-point probe method was used to measure the sheet resistances. The measurements were performed in air at room temperature. The resistances were measured at several places and an average value was calculated.

A Seiko TG–DTA instrument of the SSC 5200 series was used to study the thermal behaviour of the precursors, $La(thd)_3$ and $Ni(thd)_2$. TG and DTA curves were recorded simultaneously in a nitrogen atmosphere under 7 mbar pressure. The sample masses were *ca.* 7 mg.

X-Ray photoelectron spectroscopy measurements were performed with a Kratos Analytical Axis 165 instrument using monochromated Al-Kα radiation, 0.5 eV step and 80 eV analyser pass energy. As many films were insulating, sample surfaces were flooded with slow electrons during the acquisition. The deviation in the binding energies, due to the charge neutralisation, was corrected using the C 1s contamination peak referenced at 284.8 eV. A scanning electron microscope of type Philips XL30 was used to study the morphology and quality of the thin films. AFM measurements were made in a Nanoscope III AFM instrument. Magnetization measurements were carried out between 5 and 320 K in a magnetic field of 1 kOe with an MPMS system (Quantum Design).

Results and Discussion

Growth conditions for $LaNiO_3$ films

A major motivation for this work was to demonstrate the feasibility of making $LaNiO_3$ as a thin film in an ALE reactor. Hence, the work was concentrated on studying the growth rate as a function of deposition temperature and number of cycles, and to characterize the $LaNiO_3$ thin films thereby obtained. Atomic layer epitaxy (ALE) is a technique used for growing single crystals and thin films.[20] In this method the reactants are alternately pulsed into the reactor chamber, where the substrates are located. Between the reactant pulses any excess of the reactants is purged out with an inert gas, leaving ideally one monolayer of the reactant chemisorbed on the substrate. In practice, however, the growth per cycle is a fraction of a monolayer owing to steric and other effects.[20–22]

La–Ni–O thin films were deposited from $La(thd)_3$ and $Ni(thd)_2$ using ozone as an oxygen source. By varying the source temperatures the optimum sublimation behaviour of the La and Ni precursors was found at source temperatures of 190 and 145 °C, respectively. The precursor materials were pulsed separately, since the difference in sublimation temperature is too large to mix the solid precursors before they are sublimed. The TG–DTG–DTA recordings of the precursor materials, $La(thd)_3$ and $Ni(thd)_2$, show almost complete sublimation. $La(thd)_3$ sublimes at around 200 °C and $Ni(thd)_2$ at around 150 °C, see Fig. 1. The pressure used in these thermoanalytical studies (7 mbar) is somewhat higher than the pressure in the reactor during the depositions (0.4–1 mbar). After

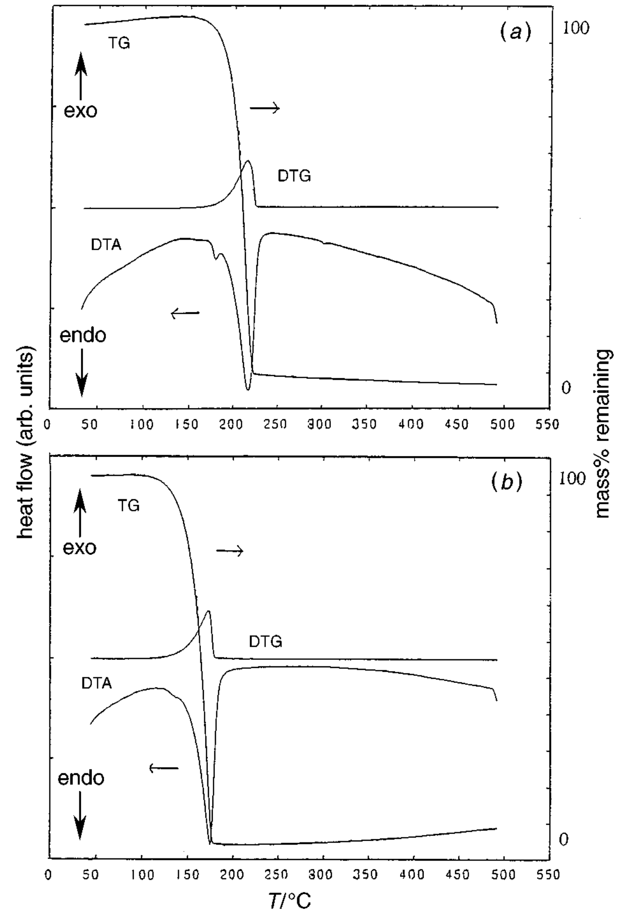

Fig. 1 TG–DTG–DTA curves for the precursors recorded with a heating rate of 10 °C min^{-1} in flowing nitrogen at 7 mbar pressure: (*a*) $La(thd)_3$ 6.5 mg, (*b*) $Ni(thd)_2$ 7.1 mg

depositions in the ALE reactor, however, there were residues in the source crucibles indicating partial decomposition during prolonged heating. The residue in the $Ni(thd)_2$ crucible was partly white–grey, different from the pink source material. In the case of $La(thd)_3$, however, there were no visible changes between the residue and the white $La(thd)_3$ source material.

The deposition temperature has a great influence on the film growth. The dependence of the film thickness on the growth temperature for depositions consisting of 272 basic cycles (272 × 30 cycles) is shown in Fig. 2. The growth rate increases as a function of temperature from 150 °C to 215 °C. In the temperature region from 215 to 250 °C the growth rate seems to be constant at 0.08 Å $cycle^{-1}$ (2.4 Å per basic cycle). This plateau shows saturation of the growth independent of the deposition temperature, which is an indication of a possible ALE window.[21] At temperatures between 250 and 400 °C the growth rate increases again indicating another reaction mechanism. For thin films deposited above 400 °C the thicknesses were not measured because of the poor film quality.

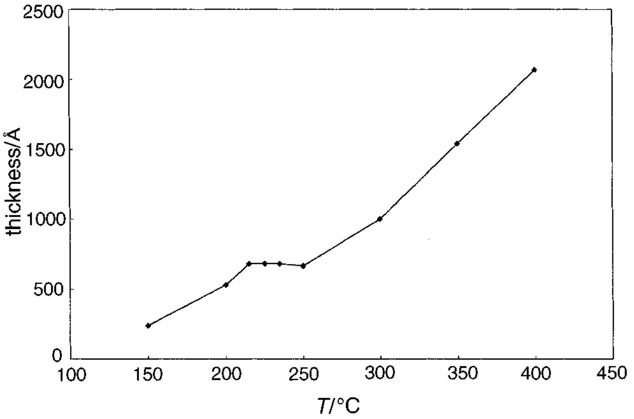

Fig. 2 Dependence of $LaNiO_3$ film thickness on the deposition temperature

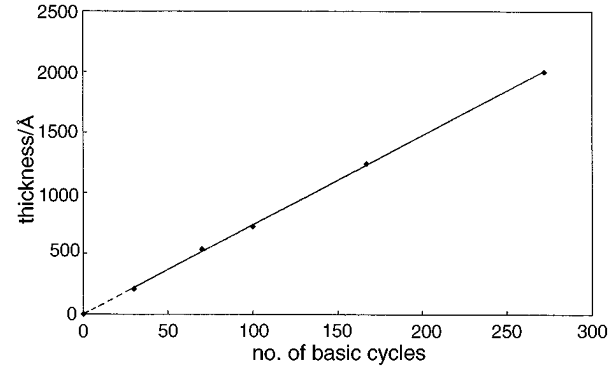

Fig. 3 Dependence of film thickness on the number of basic cycles (deposition temperature 400 °C)

The dependence of the film thickness on the number of cycles was studied at 400 °C, using the pulse durations described above. The growth rate shows an almost linear dependence on the number of cycles, see Fig. 3. The growth rate saturates to a value of 0.24–0.26 Å $cycle^{-1}$ (7.2–7.8 Å per basic cycle). This means that the thickness of the thin film can be controlled easily by the number of deposition cycles.

Characterization of as-deposited and annealed La–Ni–O films

The thin films deposited at temperatures below 450 °C are transparent and X-ray amorphous, as shown by X-ray diffraction patterns, see Fig. 4(*a*). They exhibit a range of colours, mostly from yellow to brown, but sometimes the leading edge of the substrate is almost black. The size of this black area tends to increase when the deposition temperature is lowered and thin films deposited at 150–215 °C are totally black–grey. The possible reasons for these colour variations are discussed later. Some of the thin films deposited at 450 °C are partly crystalline and all the XRD peaks can be indexed as $LaNiO_3$ reflections. The crystalline $LaNiO_3$ thin films are black and mirror-like. At higher reactor temperatures (500 °C) the films are black and much less mirror-like, and the XRD pattern indicates a phase mixture of La_2NiO_4 and NiO. This means that 450 °C is close to the upper temperature limit for successful deposition of $LaNiO_3$. This temperature is far below the observed decomposition temperature of polycrystalline $LaNiO_3$ in an oxygen atmosphere.[14,15]

The amorphous films become crystalline when heated in flowing oxygen at 600 °C for 12 h either in the reactor or in a separate tube furnace. Some crystallinity develops also for thin

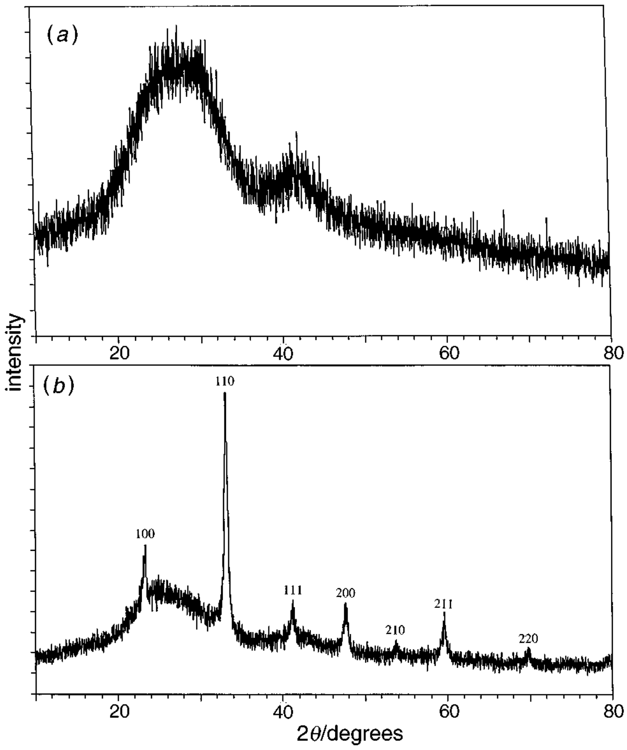

Fig. 4 Powder X-ray diffractogram (Cu-Kα radiation) of (*a*) an amorphous thin film, deposited at 400 °C, 0.4 mbar on Corning glass substrate, (*b*) an $LaNiO_3$ thin film after annealing at 600 °C for 12 h in O_2. Miller indices are given. Film thickness *ca.* 2000 Å.

films heated at 500 °C in air for 12 h; however, when treated at 400 °C in air or oxygen they remain amorphous. Simultaneously with the crystallization a colour change from yellow–brown to black occurs. The XRD patterns from the heated samples agree with that for $LaNiO_3$, see Fig. 4(*b*). The *d*-values obtained for a $LaNiO_3$ film are listed in Table 1. Compared with the powder X-ray patterns of the polycrystalline bulk materials, no splitting of reflections owing to a rhombohedral distortion ($a_{RH} = 5.395$ Å and $\alpha = 60.77°$ for $LaNiO_3$[17]) is observed. The crystalline film is therefore cubic. This is consistent with earlier reports on $LaNiO_3$ thin films deposited by other techniques.[9–11] For the $LaNiO_3$ film heated/crystallized in oxygen at 600 °C [Fig. 4(*b*)], the unit-cell parameter $a = 3.804$ Å was calculated. As seen from the Miller indices in Fig. 4(*b*) for $LaNiO_3$, there is no indication of a preferred orientation and the intensities match well those of polycrystalline $LaNiO_3$. Since Corning glass was used as the substrate, epitaxial or strongly textured films were not expected.

Table 1 Positions of Bragg reflections given as *d*-values for $LaNiO_3$ thin film crystallized at 600 °C; data from refs. 11 and 23 are included for comparison

hkl	*d*/Å[a]	*d*/Å[b]	*d*/Å[c]
100	3.809	3.816	3.850
110	2.690	2.692	2.730
111	2.187	2.192	2.229
200	1.905	1.907	1.932
210	1.703	1.708	1.728
211	1.548		1.578
220	1.345	1.348	1.365

[a]This study. [b]Ref. 11. [c]Ref. 23.

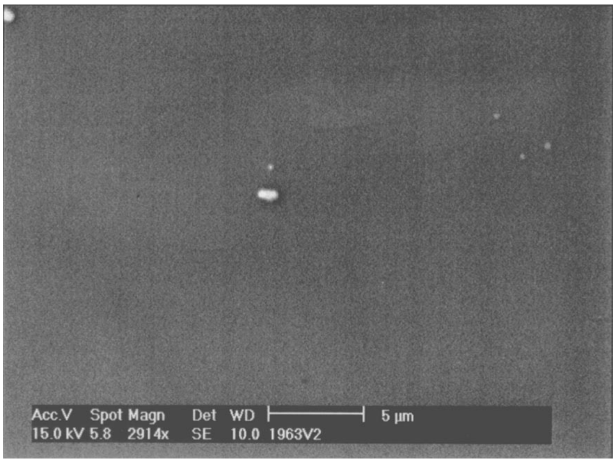

Fig. 5 SEM picture of an $LaNiO_3$ thin film deposited at 400 °C on Corning glass (pressure 0.4 mbar) and heated at 600 °C for 12 h in O_2. Film thickness *ca.* 2000 Å.

The quality and morphology of the thin films were examined by scanning electron and atomic force microscopies. SEM pictures indicate that the thin films are dense and no phase inhomogenities are evident, but various amounts of depressions and other thickness variations in the thin films are seen in some samples. The surface of the $LaNiO_3$ thin films obtained appears to be more smooth than that of $LaNiO_3$ films deposited by other methods.[9,11] Generally the SEM pictures are contourless. For some films, small amounts of spherical particles are observed, see Fig. 5. It was not possible to distinguish between the composition of the thin film and the particles. Similar particles have been reported for thin $LaNiO_3$ films made by spray combustion flame and spray-ICP techniques.[9,11] Such particles are observed for the crystalline as well as for the amorphous thin films. No obvious relation between the number of particles and the deposition parameters could be found. The SEM examinations show no significant difference between the amorphous, crystalline, yellow–brown and black films.

AFM measurements (Fig. 6) show that the as-deposited amorphous thin films contain small crystallites. The roughnesses of the as-deposited films are the same or even less than the roughness of the substrate, which is a sign of smooth growth of the amorphous thin film. No variations in microstructure due to thickness variations or different deposition temperatures were found. However, owing to annealing the crystallite size and the roughness of the films increases, see Fig. 6.

Crystallinity, colour and physical properties

The La–Ni–O films show a large range of characteristics, from amorphous to crystalline, from yellow *via* brown to black, and a five orders of magnitude variation in resistivity. In order to understand the cause of these variations a number of annealing experiments, XPS, magnetic susceptibility and resistivity studies were undertaken.

First the colour will be considered. The thin films annealed

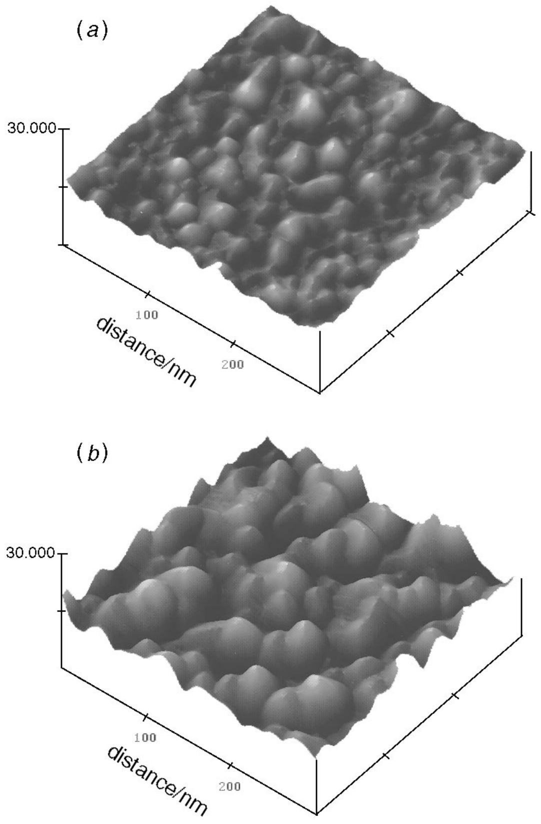

Fig. 6 Atomic force microscopy (AFM) pictures of $LaNiO_3$ thin films deposited on Corning glass at 250 °C (film thickness *ca.* 670 Å). (*a*) As-deposited, (*b*) after annealing at 600 °C for 12 h in O_2.

in O_2 at 600 °C contain $LaNiO_3$. They are black, independent of the state of the intermediate amorphous film. The reason for the yellow–brown–black colouring of the amorphous films appears unclear. The colour variations may have different causes: (i) film thickness; (ii) carbon impurities introduced from decomposed precursor; (iii) degree of crystallinity; (iv) multiphase nature of the thin films; or (v) oxygen non-stoichiometry. The first possibility can be excluded since the colour variations are found over films where the measured thickness is constant. Furthermore, some of the blackest films are actually very thin. Possibility (ii) is also unlikely, since enhanced carbon formation owing to thermal decomposition of $La(thd)_3$ and $Ni(thd)_2$ precursors is expected at the higher deposition temperatures. This is not the case since films deposited at 400 °C still have colour variations, whereas some films deposited at 200 °C are virtually black. All films deposited at temperatures below 450 °C are X-ray amorphous and turn crystalline only after thermal treatment. Hence, the colour differences are not just connected with the X-ray crystallinity of the films; however, they may still be connected with microcrystallinity.

The colour variations in the amorphous thin films could possibly be caused by a multiphase situation (iv), being due to either a mixture of La_2O_3 and NiO or other La–Ni–O phases. In order to evaluate this possibility, films of the single oxides La_2O_3 and NiO were deposited, using $La(thd)_3$ and $Ni(thd)_2$ as precursors and the same pulsing and purging times as described for deposition of the mixed oxide. The number of cycles used was 5000. Depositions of the Ni–O thin films were made at 250, 350 and 400 °C. XRD measurements show that the as-deposited Ni–O thin films were crystalline. The XRD patterns for films grown at 250 °C (1 mbar) and 350 °C (0.8 mbar) were indexed as NiO. At 400 °C (1 mbar) the thin film consisted of a mixture of NiO and Ni. The La–O thin film growth was studied in the temperature range 200–450 °C, depositions being made every 50 °C. XRD measurements show that the as-deposited thin films were crystalline when grown at temperatures between 350 and 450 °C.[24]

In order to study further the possible reasons for the changes in colour, some annealing experiments were carried out under a reducing atmosphere. In a very reducing atmosphere [CO_2–N_2–2% H_2; $p(O_2) = 10^{-24}$ bar, $T = 600$ °C], complete decomposition occurs for both amorphous and crystalline La–Ni–O films, giving in both cases dark brown films containing crystalline Ni + $La_2O_2CO_3$ (type I or IA). Under modestly reducing conditions [N_2; $p(O_2) = 10^{-4}$ bar], the yellow and brown amorphous films turn black. However, they still remain X-ray amorphous. These experiments show that the atmosphere is of great importance for obtaining a crystalline $LaNiO_3$ thin film, and further that the colour is not connected directly with the crystallinity. For La–Ni–O films converted to crystalline $LaNiO_3$ by heat treatment in oxygen, exposure to N_2 does not change the colour or the diffraction pattern. The latter experiments were conducted under normal atmospheric conditions, under which the thin film may reoxidize from a reduced state, see below. If the amorphous phase is less stable than the crystalline $LaNiO_3$ under an N_2 atmosphere, the observed changes in colour may possibly be due to decomposition of the amorphous $LaNiO_3$ phase into X-ray amorphous forms of one or more of the phases $La_2Ni_2O_5$, $La_4Ni_3O_{10}$, La_2NiO_4, $LaNiO_2$, NiO, La_2O_3 and Ni.

The range of oxygen non-stoichiometry in $LaNiO_3$ is large at low temperatures where topotactic reduction will remove oxygen from alternating sheets in the crystal structure, resulting in $La_2Ni_2O_5$ with octahedral and square-planar coordinated nickel.[25] At higher temperatures than, say, 500 °C, such reduction is no longer possible, the kinetically stable perovskite-related structure is broken up and the thermodynamically stable two-phase mixture is obtained. For topotactically reduced bulk specimens, complete reoxidation occurs at room temperature. It is therefore not very probable that the thin film should contain regions with significantly different oxygen non-stoichiometries.

As regards the electrical resistivity, it was found to vary from 3.2 Ω m for an amorphous as-deposited film to 1.8×10^{-5} Ω m for the same $LaNiO_3$ film after annealing and crystallization. The lowest resistivity observed was 5.4×10^{-6} Ω m. The latter value is slightly larger than found for spray-ICP deposited films[9] and for laser deposited $LaNiO_3$ films,[8] but probably equal within reasonable uncertainty limits. On the other hand, the resistivity is significantly lower and the minimum is obtained at lower temperature than for $LaNiO_3$ prepared by pyrolysis of spin-coated organometallic films.[13] There is no difference in resistivity between the yellow, brown and black amorphous films.

Characterization by XPS and magnetic susceptibility measurements

Characterization of the electronic state of nickel in La–Ni–O films was attempted *via* XPS and magnetic susceptibility studies. The surface chemistry of two films with and without annealing was studied with XPS. The films were deposited at 250 and 400 °C and the annealing was carried out in O_2 at 600 °C for 12 h.

As the samples were measured without any *in situ* cleaning in UHV, both carbon and oxygen contamination species were present on the surface. No other impurities were detected from the spectra. The surface concentration of nickel in the non-annealed specimen was roughly three times that of lanthanum whereas for annealed samples the amounts of lanthanum and nickel at the surface were nearly equal. As the last sequence in the growth of the films was 15 cycles of nickel and ozone precursors, the XPS results indicate that the outermost layers reacted only during the annealing when the films also changed from amorphous to crystalline.

The O 1s line shape changed markedly upon annealing (Fig. 7). The as-deposited films had two resolvable components. The broad high binding energy component at 531.3 ± 0.1 eV probably originates from the chemisorbed O^- and OH^- groups and the nickel-bound oxygen.[26–28] The low energy component at 528.7 eV was assigned to the La_2O_3 component.[29] However, the annealed films were composed of three resolvable peaks. The positions of the low and high binding energy components remained nearly unchanged (at 531.6 and 528.7 eV). The additional component at 530.0 ± 0.1 eV is in good accordance with the reported values for $LaNiO_3$.[27,28]

Since the La $3d_{3/2}$ emission interferes severely with the Ni 2p emission, both the weak Ni 3p and Ni LMM Auger emissions were also studied. In all films analysed the Ni 2p peak was very similar in shape and position to the reference spectrum of NiO film, verifying that no Ni_2O_3 was present on the surface. However, in the Ni LMM Auger signal of the annealed films (Fig. 8) a slight change in the peak shape was observed. This could be related to structural changes in the matrix.

The La $3d_{5/2}$ core-level spectra show split lines with maxima at 834.1 ± 0.3 and 838.1 ± 0.3 in agreement with the literature values for $LaNiO_3$.[26] The positions of the lines remain unaffected by the deposition temperature and annealing. Nickel interferes with the La $3d_{3/2}$ signal, but a subtle change in the splitting ratio of the La $3d_{5/2}$ component was detected after annealing the films. This could indicate changes in the conduction band electron configuration which could be due to changes in the La coordination number before and after annealing, as discussed by Burroughs *et al.*[30]

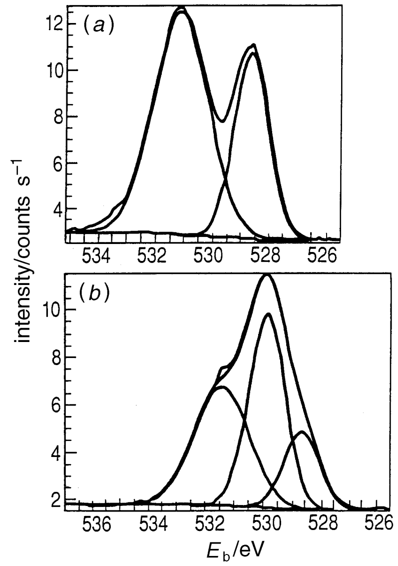

Fig. 7 XP spectra of the O 1s level of (*a*) as-deposited and (*b*) annealed $LaNiO_3$ films grown at 400 °C on a Corning glass substrate

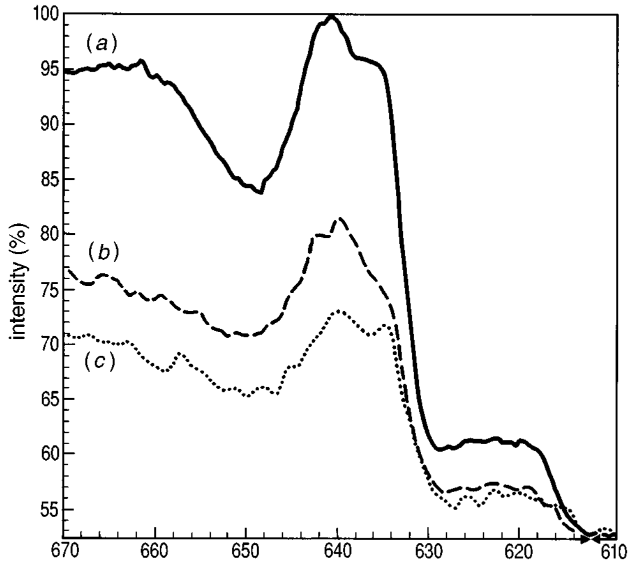

Fig. 8 XP spectra of the Ni LMM Auger level of (*a*) an NiO reference film grown at 250 °C; (*b*) as-deposited and (*c*) annealed $LaNiO_3$ films grown at 400 °C on a Corning glass substrate

Metallic $LaNiO_3$ is reported to be Pauli paramagnetic.[8] Any presence of reduced Ni^{II} species will add an additional Curie–Weiss contribution to the susceptibility. Sagoi *et al.*[8] reported, for $LaNiO_3$ deposited at 700 °C, the presence of 16% Ni^{II}, whereas in the low-resistivity films they observed no Curie–Weiss contribution from Ni^{II}. The present susceptibility measurements were performed on small pieces of the substrate coated with the La–Ni–O film. Two approaches were used:

the first involved measurement of the substrate plus film, then removal of film by treatment with hydrochloric acid and subtraction of the measured signal for the pure substrate; the second method was a simple comparison between as-measured susceptibilities without subtraction of the contribution from the glass substrate. The magnetic susceptibility curves for the as-deposited film at 400 °C are very similar to those observed for a film annealed subsequently at 600 °C in O_2. All curves show a small Curie–Weiss contribution. This indicates that the as-deposited films contain the same amount of reduced nickel species. For all samples a more or less clear cusp appear in $\chi(T)$ around 50 K. It is possible that a similar, but less pronounced, peak is also present in the data of Xu *et al.*[31] In the study by Sreedhar *et al.*[32] it is not possible to observe this peak, but the reason for this might be few measuring points in the relevant temperature range. The feature is hardly present in the as-deposited La–Ni–O at 400 °C, however, becoming very pronounced after crystallization and oxidation. It is believed that the feature is due to adsorbed oxygen.[33]

Conclusions

Thin film growth of $LaNiO_3$ by an ALE process has been demonstrated from β-diketonate type precursors and ozone. Even a very low deposition temperature of 250 °C can be used but crystallization requires annealing at 600 °C. The annealed films show metallic behaviour and are black, in contrast to the yellow colour and high resistivity of the as-deposited amorphous films. The XP spectra indicate that the amorphous as-deposited thin films consist of separate oxide layers with La–O and Ni–O character. These separate layers will react during annealing and form the crystalline perovskite structure.

Financial support from Norsk Hydro A/S and NorFa and the Academy of Finland is gratefully acknowledged. We also thank Dr. Leena-Sisko Johansson for performing the XPS measurements and aiding their interpretation as well as Mr. Mikko Utriainen, MSc, for the AFM measurements.

References

1 N. Q. Minh, *J. Am. Ceram. Soc.*, 1993, **76**, 563.
2 *Properties and Applications of Perovskite-type Oxides*, ed. L. G. Tejuca and J. L. G. Fierro, Marcel Dekker, New York, 1992, ch. 10–17.
3 U. König, O. Blum, R. Christ and I. Reeh, *J. Phys. Chem.*, 1993, **97**, 488.
4 R. N. Singh, L. Bahadur, J. P. Pandey and S. P. Singh, *J. Appl. Electrochem.*, 1994, **24**, 149.
5 A. Mackor, T. P. M. Koster, J. G. Kraaijkamp, J. Gerretsen and J. P. G. M. van Eijk, *Proc. 2nd Int. Symp. Solid Oxide Fuel Cells*, The Electrochemical Society, Pennington, NJ, 1991, p. 463.
6 J. Mizusaki, S. Yamauchi, K. Fueki and A. Ishikawa, *Solid State Ionics*, 1984, **12**, 119.
7 K. M. Satyalakshmi, R. M. Mallya, K. V. Ramanathan, X. D. Wu, B. Brainard, D. C. Gautier, N. Y. Vasanthacharya and M. S. Hedge, *Appl. Phys. Lett.*, 1993, **62**, 1233.
8 M. Sagoi, T. Kinno, T. Hushimoto, J. Yoshida and K. Mizushima, *Appl. Phys. Lett.*, 1993, **62**, 1833.
9 H. Ichinose, M. Nagano, H. Katsuki and H. J. Takagi, *J. Mater. Sci.*, 1994, **29**, 5115.
10 H. Ichinose, Y. Shiwa and M. Nagano, *Jpn. J. Appl. Phys.*, 1994, **33**, 5903.
11 H. Ichinose, Y. Shiwa and M. Nagano, *Jpn. J. Appl. Phys.*, 1994, **33**, 5907.
12 C. C. Yang, M. S. Chen, T. J. Hong, C. M. Wu and J. M. Wu, *Appl. Phys. Lett.*, 1995, **66**, 2643.
13 A. Li, C. Ge and P. Lü, *Appl. Phys. Lett.*, 1996, **68**, 1347.
14 H. Obayashi and T. Kudo, *Jpn. J. Appl. Phys.*, 1975, **14**, 330.
15 H. Fjellvåg, O. H. Hansteen, B. Gilbu, A. Olafsen, N. Sakai and H. Seim, *Thermochim. Acta*, 1995, **256**, 75.
16 S. Rakshit and P. S. Gopalakrishnan, *J. Solid State Chem.*, 1994, **110**, 28.
17 M. Crespin, P. Levitz and L. J. Gatineau, *J. Chem. Soc., Faraday Trans. 2*, 1983, **79**, 1181.
18 L. Niinistö, M. Ritala and M. Leskelä, *J. Eng. Mater.*, in press.
19 T. Suntola, A. Pakkala and S. Lindfors, *US Pat.*, 4 389 973, 1983.
20 M. Leskelä and L. Niinistö, in *Atomic Layer Epitaxy*, ed. T. Suntola and M. Simpson, Blackie and Son Ltd., Glasgow, 1990, p. 1.
21 T. Suntola, in *Handbook of Crystal Growth*, ed. D. T. J. Hurle, Elsevier, Amsterdam, 1994, vol. 3, p. 601.
22 H. Mölsä and L. Niinistö, *Mater. Res. Soc. Symp. Proc.*, 1994, **335**, 341.
23 JCPDS file 33-710; H. Wustenberg, Hahn Inst. für Kristallogr., Technische Hochschule Aachen, Germany.
24 H. Seim, M. Nieminen, H. Fjellvåg and L. Niinistö, unpublished work.
25 T. Moriga, O. Usaka, T. Imamura, I. Nakabayashi, I. Matsubara, T. Kinouchi, S. Kikkawa and F. Kanamaru, *Bull. Chem. Soc. Jpn.*, 1994, **67**, 687.
26 J. Choisnet, N. Abadzhieva, P. Stefanov, D. Klissurski, J. M. Bassat, V. Rives and L. Minchev, *J. Chem. Soc., Faraday Trans.*, 1994, **90**, 1987.
27 J. L. G. Fierro and G. Tejuca, *Appl. Surf. Sci.*, 1987, **27**, 453.
28 L. G. Tejuka and J. L. G. Fierro, *Thermochim. Acta*, 1989, **147**, 361.
29 J. F. Moulder, W. F. Stickle, P. E. Sobol and K. D. Bomben, in *Handbook of X-Ray Photoelectron Spectroscopy*, ed. J. Chastain and R. C. King, Eden Prairie, Minnesota, 1995, p. 261.
30 P. Burroughs, A. Hamnett, A. F. Orchard and G. Thornton, *J. Chem. Soc., Dalton Trans.*, 1976, 1686.
31 X. Q. Xu, J. L. Peng, Z. Y. Li, H. L. Ju and R. L. Greene, *Phys. Rev. B*, 1993, **48**, 1112.
32 K. Sreedhar, J. M. Honig, M. Darwin, M. McElfresh, P. M. Shand, J. Xu, B. C. Crooker and J. Spalek, *Phys. Rev. B*, 1992, **46**, 6382.
33 Z. Zhang and M. Greenblatt, *J. Solid State Chem.*, 1995, **117**, 236.

Paper 6/06316K; *Received* 13*th September*, 1996