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Preparation and Characterisation of $LaNi_xCo_{1-x}O_3$ Thin Films on Polycrystalline Al_2O_3-substrates

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Abstract

The perovskite $LaNi_xCo_{1-x}O_3$ exhibits metallic conductivity with a change from p- to n-type conduction around x = 0·5, thus being a candidate for electrodes or buffer layers in thin film technology. Thin films of $LaNi_xCo_{1-x}O_3$ have been grown onto polycrystalline Al_2O_3 substrates by Chemical Solution Deposition (CSD) of nitrate solutions in ethanol/butylacetate. The solutions were applied by dip-coating. After pyrolysis the compounds are formed in air at temperatures between 600°C and 750°C. Formation of the perovskite phase was confirmed by grazing angle X-ray diffraction. Electron micrographs revealed that the obtained films were smooth and crack-free and consisted of nanocrystalline $LaNi_xCo_{1-x}O_3$ particles. The thickness of the films was between 200 nm and 400 nm, depending on the conditions of the dipcoating procedure. Specific conductivities of the film were measured using the van der Pauw-method and were found to be around 400 S/cm for $LaNiO_3$ and around 1 S/cm for $LaCoO_3$ at room temperature. © 1999 Elsevier Science Limited. All rights reserved

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1 Introduction

From the large number of perovskite oxides with high electronic conductivity, the system $LaNi_xCo_{1-x}O_3$ is one of the most promising materials for electrode purposes. $LaNiO_3$ is reported to be a n-type conductor with a conductivity up to 10^3 S/cm.[1,2] Its application as thin film electrode for ferroelectric memory devices has raised more and more interest during the last years.[3–5] $LaCoO_3$ is a p-type semiconductor with complex electrical behaviour.[6,7] In the homologous series of $LaNi_x$-$Co_{1-x}O_3$ electrical characteristics can be tuned by composition. The Seebeck coefficient varies with composition and changes its sign around $x = 0{\cdot}5$ indicating a change from n- to p-type conductivity.[8] Also thermal stabilities of the compounds increase with x. $LaNiO_3$ decomposes in air at 860°C,[9] whereas $LaNi_{0{\cdot}6}Co_{0{\cdot}4}O_3O_3$ was found to be stable up to 1300°C.[8] Up to now chemical solution deposition (CSD) of $LaNiO_3$ thin films on various substrates has been done by metal-organic decomposition (MOD) for example of carboxylates dissolved in xylene.[3] The aim of this work is the structural, morphological and electrical characterisation of $LaNi_xCo_{1-x}O_3$ thin films obtained by a CSD route from nitrate solutions.

2 Experimental

For the CSD-processing of $LaNi_xCo_{1-x}O_3$ the compounds $La(NO_3)_3{\cdot}6H_2O$, $Ni(NO_3)_2{\cdot}6H_2O$ and $Co(NO_3)_2{\cdot}6H_2O$ (Merck, analytical grade) were

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dissolved in appropriate ratios in a mixture of ethanol/butylacetate (1:4) to yield 0·25 molar solutions. No further treatment of the solution (removal of water) was carried out. As the substrates, polycrystalline Al_2O_3 plates with a thickness of 0·63 mm, were used. The substrates were coated by dipping into the solution. After careful drying the samples were rapidly heated to 530 °C for one hour for the pyrolysis of the components. In a final step the samples were annealed at 790 °C in air for one hour. The prescribed film thickness was obtained by three times repeating the coating process.

The obtained phase was identified by X-ray diffraction in grazing angle technique using a powder diffractometer (SIEMENS D5005) with Cu-Kα radiation. Morphology of the films of freshly broken samples without any coating was investigated by scanning electron microscopy (Leo 982 Gemini). Composition and average film thickness was determined by EDX-measurement. The electrical conductivity was measured as a function of temperature using the van der Pauw-method (four point measurement). To improve the electrical contact between the probes and the sample dots of silver Paint (DEMETRON) were deposited on the samples.

3 Results and Discussion

The X-ray powder diffraction patterns (pattern of $LaNiO_3$ in Fig. 1) of the specimen show broad but distinct peaks of the perovskite phase beside sharp substrate peaks. The peak broadening is obviously due to the nano-sized particles that make up the film. The film morphology is illustrated in the SEM-images (Figs 2–4). Figure 2 shows a polycrystalline $LaNi_{0.6}Co_{0.4}O_3$-film on the Al_2O_3-substrate. It illustrates the microstructure of the substrate and the complete covering of the surface by the perovskite film. The uniformity of the film thickness is disturbed by the uneven surface of the substrate. Figure 3 is a

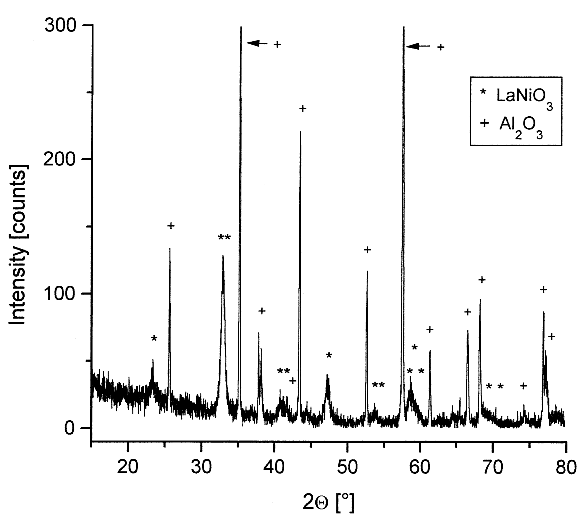

Fig. 1. XRD-pattern of a $LaNiO_3$-film on a Al_2O_3-substrate in grazing angle technique.

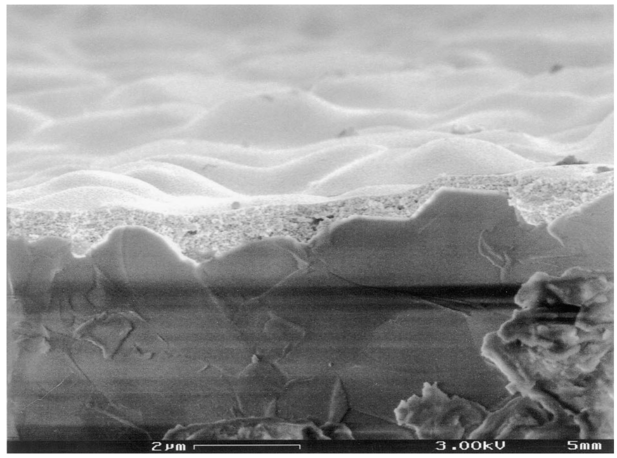

Fig. 2. SEM image of a polycrystalline $LaNi_{0.6}Co_{0.4}O_3$ film on a Al_2O_3-substrate (bottom).

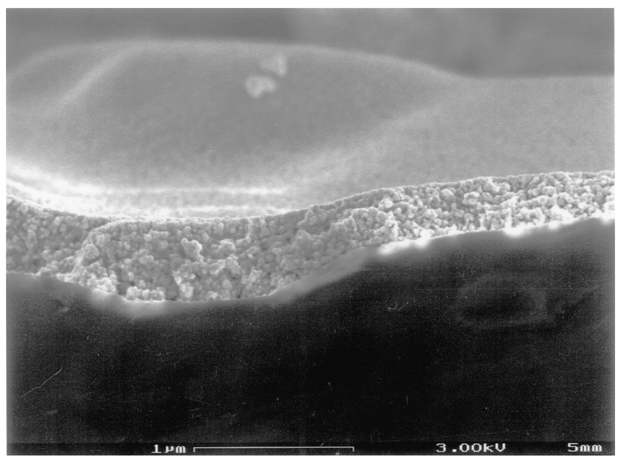

Fig. 3. SEM image of a polycrystalline $LaNiO_3$-film on a Al_2O_3-substrate (bottom).

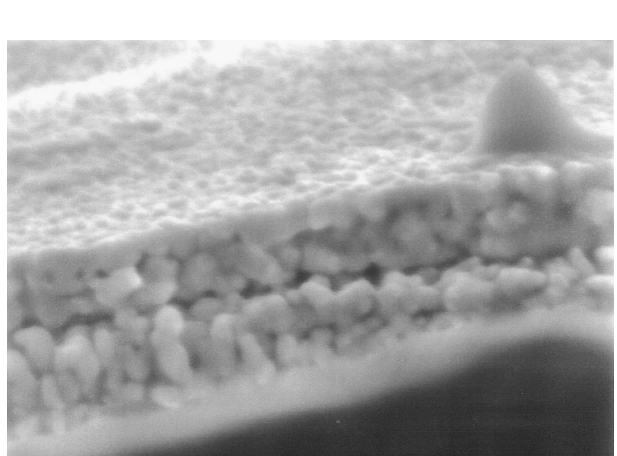

Fig. 4. SEM image of a polycrystalline $LaCoO_3$-film on a Al_2O_3-substrate (bottom).

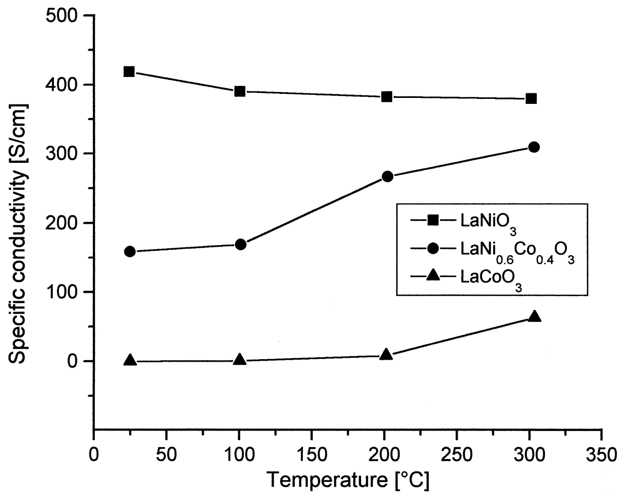

Fig. 5. Specific conductivity versus temperature of $LaNi_xCo_{1-x}O_3$-films.

SEM-image of a $LaNiO_3$-film with a higher magnification. The uniform grain size distribution of the perovskite particles and a certain amount of porosity becomes visible. More clearly this can be seen in Fig. 4, a SEM-image of a $LaCoO_3$-film. Generally it can be said that the films are crack-free but show some voids which might be due to dust particles on the surface before calcination. The films contain a certain amount of porosity which decreases with increasing cobalt content. Grain size seems to increase with increasing cobalt content ranging from 50 to 100 nm.

Because of the great variation of the film thickness due to the substrate morphology, an average film thickness was measured by EDX comparing the intensity of an element line from the film with the intensity obtained from a massive element standard considering atomic number as well as absorption correction in an iterative calculation. The average thickness determined for the $LaNiO_3$- and the $LaNi_{0.6}Co_{0.4}O_3$-film was 390 nm, the average thickness determined for the $LaCoO_3$-film was 225 nm. These values were taken for the calculation of the specific conductivity from the van der Pauw-measurements. The conductivity data are shown in Fig. 5. As expected conductivity decreases, with increasing cobalt content. The $LaNiO_3$-film shows the highest conductivity with the typical temperature dependence of a metallic conductor. The conductivity amounts to one half to one third of the literature values[1,2] of the bulk material but is in good agreement with the conductivities of $LaNiO_3$ thin films on silicon substrates.[3] A surprising feature is the strong temperature dependence of the conductivity of the $LaNi_{0.6}Co_{0.4}O_3$-film since this material should exhibit metallic properties as well.[8]

4 Conclusions

In this work it could be demonstrated that highly conductive films of the $LaNi_xCo_{1-x}O_3$ series can be obtained by a simple CSD-process from nitrate solutions. The substrate is completely covered by a smooth and crack free polycrystalline film. The grain size distribution within the film is quite uniform, no abnormal or oriented growth can be observed. An appreciable film thickness between 200 and 400 nm can be achieved by a single coating process.

Conductivity values and the composition dependence of the conductivity are in accordance with literature.

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