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Preparation of La_2NiO_4 films by d.c. sputtering on cubic ZrO_2

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Cubic ZrO_2 is a promising material for solid electrolyte fuel cells because of its high ionic conductivity at high temperatures [1, 2]. The cathode materials for cubic ZrO_2 fuel cells require permeability for oxygen, high electrical conductivity and stability in an air atmosphere at a temperature range of 1073 to 1273 K [1, 3]. The La perovskite oxides such as $LaCoO_3$, $LaMnO_3$ and their mixed oxides are candidates for cathode materials for use in cubic ZrO_2 fuel cells to fulfil the above requirements. One problem involved in the use of perovskite-type oxides for cathode material may be their reaction with the cubic ZrO_2 [4, 5]. Actually, $LaCoO_3$ reacts with cubic ZrO_2 at the interface, and the reaction produces a compound of $La_2Zr_2O_7$. The compound of $La_2Zr_2O_7$ is an insulator, even at a temperature of 1273 K [5], so that control of the reaction and the reaction products is necessary when using perovskite-type oxides for cathode materials [6]. La_2NiO_4 is also a perovskite-type oxide with high electrical conductivity and its properties are well known [7]. As La_2NiO_4 is a candidate for use as an electrode material for cubic ZrO_2 fuel cells, it is of interest to investigate the formation of thin films of this material and their changes of phase and electrical resistivity by annealing.

Thin film electrodes have usually been used as a contact material in cubic ZrO_2. The sputtering method is employed to deposit oxides consisting of several elements, because the compositional deviation of deposits can be minimized more than when vacuum deposition processing is used. In this letter we report the formation of films of La_2NiO_4 on a Y-stabilized ZrO_2 substrate by the d.c. sputtering method and the change of structure and electrical resistivities by annealing.

The starting materials were powders of La_2O_3 (99.99%) and Ni (99.9%). The La_2NiO_4 target, 25 mm in diameter, was obtained by sintering the powders at a temperature of 1573 K for 86 ks [5]. Preliminary experiments revealed that a stoichiometric composition can be obtained by sputtering under a d.c. voltage of 1.5 kV in an argon atmosphere of 4 Pa. The distance between target and substrates was about 50 mm. Two kinds of substrates were used. One is a single crystal of 10 mol% Y_2O_3–ZrO_2 which was cut and polished on its (100) plane. The other was an air-cleaved (100) KCl crystal. La_2NiO_4 was deposited at a thickness of about 3 μm on substrates at room temperature.

Electron probe microanalysis (EPMA) was employed to analyse the composition of films and the reaction in the film–substrate system. Thin film analysis was carried out by a transmission electron microscope (TEM) equipped with an energy dispersive X-ray spectroscope (EDS) (Hitachi H-800, Kevex 7500).

The electrical resistivity was measured by the conventional two-point method for as-deposited and annealed films. The annealing was carried out at temperatures of 873–1473 K in an air atmosphere.

Fig. 1 shows the annealing temperature dependence of resistivity of a 3 μm thick La_2NiO_4 film on cubic ZrO_2 substrate. Annealing in air results in a drastic decrease of the resistivity from 10 Ω cm of an as-deposited film to 10^{-2} Ω cm of an annealed film at temperatures in the range 873–1173 K. The resistivity of the annealed films at this temperature range is almost the same value as the resistivity obtained from the bulk material of La_2NiO_4 [7]. Above a temperature of 1300 K, the resistivity once again increased.

Fig. 2 shows an electron diffraction pattern of an as-deposited film at a substrate temperature of

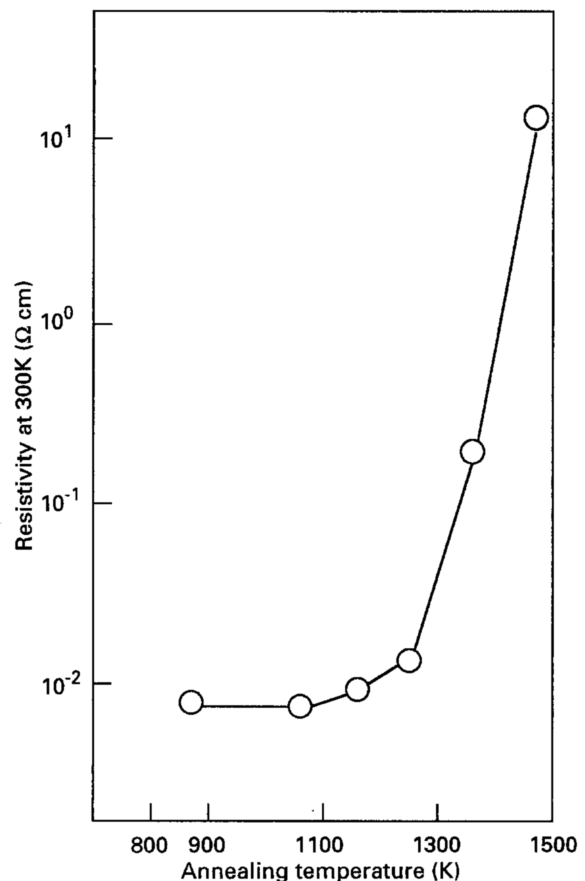

Figure 1 Annealing temperature dependence of electrical resistivities of 3 μm La_2NiO_4 films on (001) cubic ZrO_2 substrates. (O), As-deposited.

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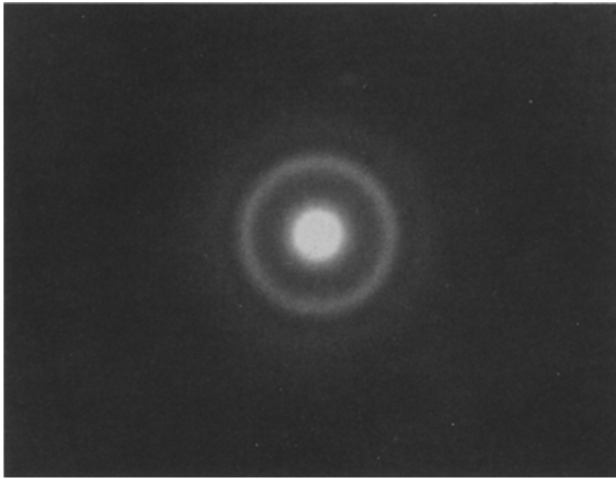

Figure 2 Electron diffraction pattern of as-deposited film.

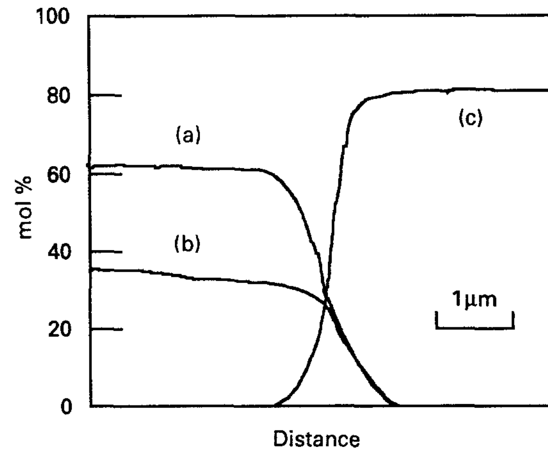

Figure 3 Cross-sectional line analysis of annealed film at a temperature of 1073 K for 86.4 ks. (a) La, (b) Ni and (c) Zn.

300 K using the La_2NiO_4 target. This electron diffraction pattern shows halo rings, i.e. the structure of an as-deposited film is amorphous. This usually occurs when the d.c. sputter-deposition of ceramics is performed at a substrate temperature around room temperature [8]. The composition of an as-deposited film was estimated as La/Ni = 2/1 from the EDS analysis using TEM. This experimental result shows that an amorphous film of La_2NiO_4 has a high electrical resistivity even though it is of stoichiometric composition.

Fig. 3 shows a cross-sectional EPMA profile of the La_2NiO_4 film/c-ZrO_2 system after annealing at a temperature of 1073 K for 86.4 ks, at which the annealed film of La_2NiO_4 exhibits the minimum value of resistivity. The EPMA analysis suggests that the film consists of a single phase of La_2NiO_4, which may be the reason why the resistivity shows a relatively low value. Fig. 4 shows the electron micrograph and the electron diffraction pattern of a section parallel to the interface between La_2NiO_4 and a cubic ZrO_2 single crystal annealed at 1173 K for 86.4 ks. The electron diffraction pattern consists of (0 0 1) cubic ZrO_2 and polycrystalline La_2NiO_4. Careful inspection of the electron diffraction reveals the splitting of reflections of cubic ZrO_2. The compound of La_2NiO_4 is seen to have a tetragonal structure with a lattice parameter of $a = 0.38551$ nm and $c = 1.2652$ nm [7]. Because the lattice spacing of (1 1 0) La_2NiO_4 has almost the same value as that of (2 0 0) cubic ZrO_2 [9], i.e. the misfit between them is about 6.9%, the splitting of the reflections of cubic ZrO_2 is caused by the epitaxial growth of La_2NiO_4 on cubic ZrO_2 during the recrystallization from the amorphous phase. The orientation relationship between La_2NiO_4 and cubic ZrO_2 is (0 0 1)L//(0 0 1)Z and [1 1 0]L//[1 0 0]Z, where L and Z indicate La_2NiO_4 cubic ZrO_2, respectively. The estimation of misfit from the electron diffraction pattern is in good agreement with that obtained by the calculation from lattice parameters. The bright field image of the plane-view section of the interface reveals the misfit dislocations which are caused by the accommodation of lattice mismatch between La_2NiO_4 and cubic ZrO_2. Dislocation lines are in the $\langle 1 1 0 \rangle$ directions with the spacing of 5 nm, which corresponds to the spacing of a misfit dislocation of cubic ZrO_2 with the Burger's vector of a[1 1 0]/2. On the other hand, the grains without dislocations seems to correspond to La_2NiO_4 grains having orientation relationships other than (0 0 1)L// (0 0 1)Z and [1 1 0]L//[1 0 0]Z. It is difficult to determine the orientation relationships, except the above

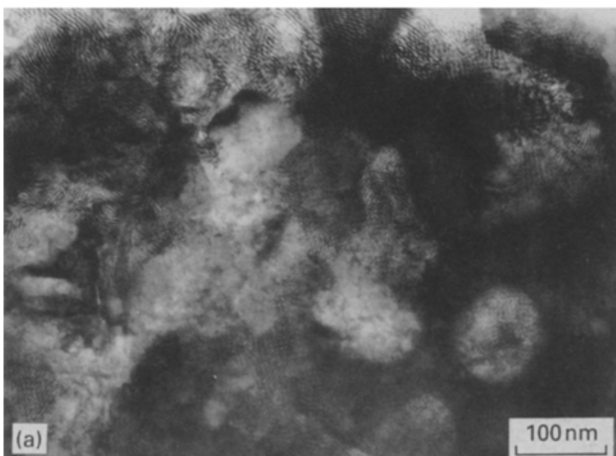

Figure 4 (a) Electron micrograph and (b) electron diffraction pattern taken from section parallel to interface between La_2NiO_4 and (0 0 1) cubic ZrO_2 after annealing at a temperature of 1173 K for 86.4 ks.

well defined relationship, because the diffraction pattern shown in Fig. 4b includes so many reflections of La_2NiO_4 randomly distributed. The temperature of 1173 K seems to be the maximum temperature at which La_2NiO_4 can be used as thin film electrode material for cubic ZrO_2. Above a temperature of 1273 K, the resistivity increased due to the reaction of the La_2NiO_4 film with cubic ZrO_2 substrate and the production of insulating material of $La_2Zr_2O_7$ [5].

References

1. P. HAGENMULLER and W. VAN GOOL (editors), "Solid electrolytes" (Academic Press, New York, 1978).
2. "High temperature solid oxide electrolytes" (Upton, New York, 1983).
3. C. S. TEDMAN, Jr, H. S. SPACIL and S. P. MITOFF, *J. Electrochem. Soc.* **116** (1969) 1170.
4. O. YAMAMOTO, Y. TAKEDA, R. KANNO and M. NODA, *Solid St. Ionics*, **22** (1987) 241.
5. J. ECHIGOYA, S. HIRATSUKA and H. SUTO, *Mater. JIM* **30** (1988) 634.
6. J. ECHIGOYA and K. NARIA, *Phys. Status Solidi A* **122** (1990) 87.
7. P. ODIER, Y. NIGARA and J. COUTURES, *J. Solid St. Chem.* **56** (1985) 32.
8 A. KINBARA and H. FUJIWARA, "Thin films" (1979), (Shokabo, Tokyo, 1979) in Japanese.
9. R. S. ROTH, *J. Res. Natl. Bureau Standards* **56** (1956) 2643.

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