Effects of Ru Co-Sputtering on the Properties of Porous Ni Thin Films

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ABSTRACT

NiO films and Ru co-sputtered NiO films were deposited by reactive magnetron sputtering for micro-solid oxide fuel cell anode applications. The deposited films were reduced to form porous films. The reduction kinetics of the Ru doped NiO film was more sluggish than that of the NiO film, and the resulting microstructure of the former exhibited finer pore networks. The possibility of using the films for the anodes of single chamber micro-SOFCs was investigated using an air/fuel mixed environment. It was found that the abrupt increase in the resistance is suppressed in the Ru co-sputtered film, as compared to undoped film.

Key words: NiO, Ni, Ru co-sputtering, Porous thin film, Solid oxide fuel cell anode

1. Introduction

R ecently, interest in the use of mini- and micro-SOFCs for portable power generation has increased.[1-4] A micro-SOFC (μ-SOFC) has several distinct advantages over batteries in that it has a much higher power density and does not require a lengthy recharging time. Therefore, if a microfabricated fuel cell could be integrated with other electronic circuits, it would expand the possibility of the operation of portable devices.[1] However, the operation temperature of a conventional SOFC is typically very high (≥800°C), which is a constraint associated with several issues, such as cell degradations due to interface reactions and thermal expansion mismatches among components such as electrodes, electrolytes, and sealants. Especially for microfabricated cells, this temperature is exceedingly high for the maintenance of the cell structure, and for this reason the operation temperature should be lower. Furthermore, a cell design more resistant to thermal shock should be studied. In this regard, single chamber SOFCs are particularly attractive, as their design can be simplified to a great extent without using sealants, which can make single chamber fuel cells more thermal shock resistant.[4]

For the single chamber operation, SOFCs are placed in an air-fuel mixture environment. In this environment, the stability of the electrodes becomes more important for reliable operations. Currently, nickel is the most commonly used material for the anode of SOFCs. This is due to economical reasons and because of the catalytic activity of a Ni anode in the operation temperature range of SOFCs.[5-7] A require-

ment for Ni anodes is a sufficient porosity to ensure gas transport to the reaction sites that correspond to the interface between the Ni anode and the electrolyte in order to increase the efficiency of the cell operation. Moreover, the stability and the selectivity regarding the fuel of a Ni-based anode in an air-fuel mixed ambient environment becomes important for the single chamber operation. In this regard, Ru doping into the Ni anode appears as an attractive approach, as Ru enhances catalysis of the partial fuel oxidation and is more resistant to oxidation in a mixed air environment.[8]

Hence, in this work the effect of Ru doping in Ni thin films was examined by co-sputtering Ru with NiO for application as anodes in single chamber μ-SOFCs. Two types of films were compared. The first were films deposited by sputtering only NiO, and the second were films deposited by co-sputtering. Porous thin films were successfully fabricated by reducing sputter-deposited films. The stability of the films in the single chamber operation is discussed based on an impedance analysis of the deposited films in the air-methane mixed environment. The differences in the physical and electrical properties between the films are also discussed.

2. Experimental Details

$Al_2O_3/SiO_2/Si$ (100) and a 100 nm-thick Gd_2O_3-doped CeO_2 (GDC) covered $Al_2O_3/SiO_2/Si$ (100) substrate were used in the experiments. 150 nm-thick Al_2O_3 layers were deposited using an e-beam evaporation method on thermal SiO_2 (1 μm) covered Si (100) substrates. GDC thin films were deposited by DC and RF reactive co-sputtering of metal Gd and Ce targets in oxygen/argon ambient.[9] The power of DC (Gd) and RF (Ce) during the deposition was 10 W and 100 W, respectively. The deposition was performed at room temper-

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ature and the working pressure was 11 mTorr. The measured growth rate of the GDC thin film was 1.4 nm/min at an O_2/Ar gas ratio of 0.1 (3 sccm/30 sccm). The chemical composition of the deposited GDC film was measured via an AES analysis.

NiO and Ru co-sputtered NiO thin films were deposited on both Al_2O_3/SiO_2/Si(100) and GDC/Al_2O_3/SiO_2/Si(100) substrates by RF sputtering at various O_2/Ar ratios. The O_2/Ar ratios were controlled by changing the flow rates of each gas at a fixed ambient pressure of 5 mTorr. A 4-inch NiO target was sputtered at room temperature with an RF sputtering power of 300 W. For Ru co-sputtering, a Ru metal target with a purity of 99.99% was DC sputtered at the power of 40 W along with the NiO sputtering. After the deposition, the films were annealed at 400°C for up to 20 min in 4% H_2 atmosphere for reduction.

To confirm the crystallinity and the phase of the thin films, X-Ray Diffraction (XRD, Rigaku, CuK_α) measurements were carried out. The surface morphologies and thickness of the thin films were observed by Scanning Electron Microscopy (SEM, Philips, V_{acc} = 15 kV). The reduction and re-oxidation behavior of films in H_2 and the CH_4/O_2 (R_{mix} = 2) mixed ambient atmosphere were investigated by AC impedance spectroscopy (SI 1287 and SI 1260, Solartron). The impedance analysis was performed on NiO films deposited onto Al_2O_3 covered substrates in order to investigate the property of the films without the interference from the electrolyte (GDC). The measurement frequency ranged from 0.1 Hz to 10 MHz.

3. Results and Discussion

Fig. 1 shows XRD spectra of the NiO and Ru co-sputtered NiO films deposited at an O_2/Ar gas ratio of 0.3 on GDC/Al_2O_3/SiO_2/Si(100) substrates after reduction in 4% H_2. After only 5 min of reduction, the NiO thin films completely reduced and exhibited no NiO peaks, while both Ni and NiO
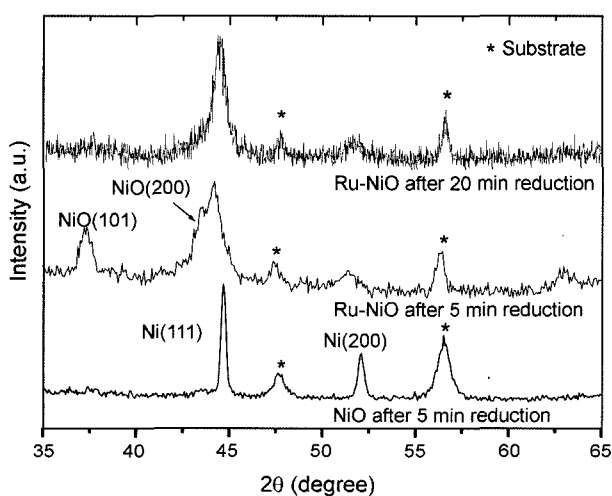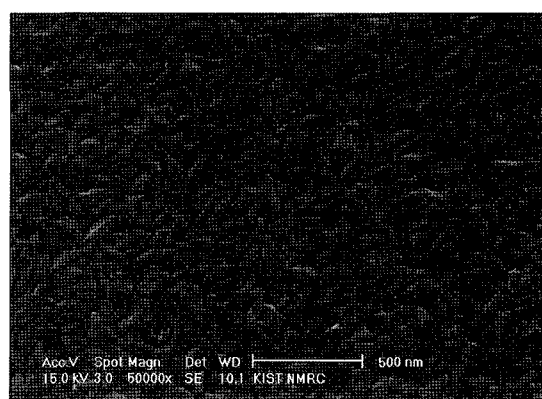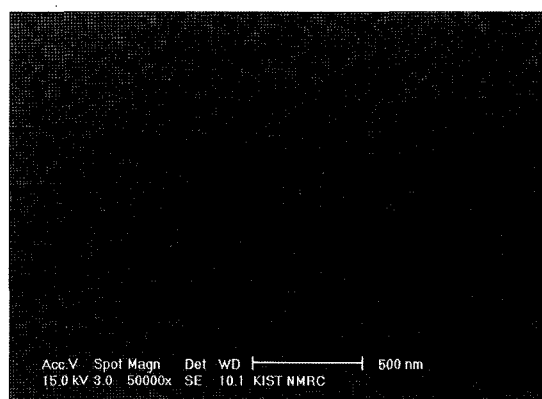
(a)

(b)

Fig. 2. Surface microstructures of as-deposited (a) NiO and (b) Ru co-sputtered NiO thin films.

Fig. 1. XRD results of NiO and Ru co-sputtered NiO thin films after reduction.

peaks were detected in the Ru co-sputtered NiO thin film. When the reduction time was increased to 20 min, NiO peaks disappeared in the XRD spectrum of the reduced Ru co-sputtered NiO films. This indicates that the reduction kinetics of NiO in Ru co-sputtered films is more sluggish than that of NiO in a film without Ru.

Surface morphologies of the as-deposited NiO and Ru co-sputtered NiO thin films are shown in Fig. 2. Both of the films exhibit continuous and homogeneous surface microstructures; however, the shapes of the grains are different for each film and the grain size of the Ru co-sputtered NiO film is smaller than that of the NiO film. This microstructural difference is caused by a change in the nucleation and growth kinetics during sputtering. As the Ru is co-sputtered to a growing film, the NiO layer contains Ru in addition to the Ni and O atoms. When a fraction of heavy element (M_{Ru} = 101) is added during the sputtering of a light element (M_{Ni} = 58), the net energetic bombardment effect[9] is amplified, resulting in an increase in the sputtering yield and supersaturation for nucleation. Finally, the Ru co-sputtered NiO film showed a finer microstructure compared to the NiO films without Ru. The other possibility is segregation of Ru. It is possible to postulate that Ru prefers to segregate at the NiO grain boundaries and thus retards the grain
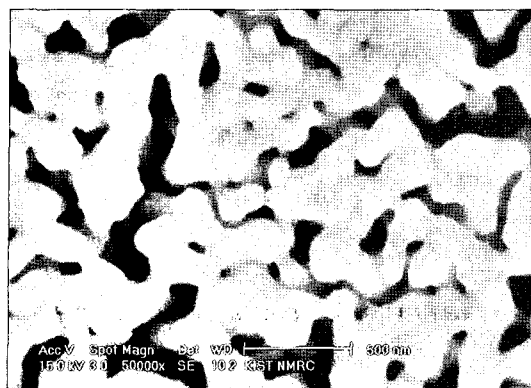
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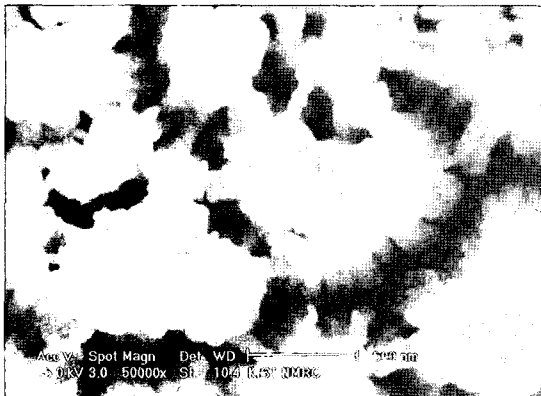
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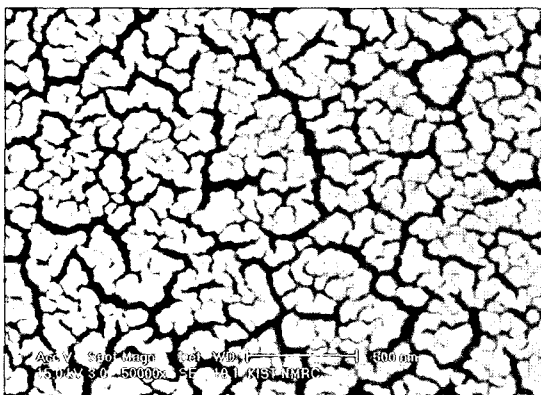
(c)

Fig. 3. SEM micrographs of (a) NiO film and (b) Ru co-sputtered NiO film reduced at 400°C for 5 min, and (c) Ru co-sputtered NiO film reduced for 20 min at 400°C in a 4% H_2 atmosphere.

growth. Further investigation is under progress in order to elucidate the effects of Ru on the microstructures more clearly.

Fig. 3 shows the surface morphologies of the films after reduction. As shown in Fig. 3(a), a porous network was developed in the NiO film annealed at 400°C for 5 min in the 4% H_2 atmosphere. The pores are likely connected throughout the thickness of the film and the surface of the GDC is exposed along the pore networks, which is essential

for a SOFC electrode to increase the triple phase boundaries formed at the conjunction of the electrode, electrolyte, and pore. However, as the pore structure develops during reduction, the adhesion of the Ni film on GDC deteriorated and delamination of the films frequently occurred. Fig. 3(b) shows the surface morphology of the Ru co-sputtered NiO film after 5 min of reduction. Contrary to what is shown in Fig. 3(a), the porous network is not fully developed after identical time durations. The surface is covered mostly with large continuous areas of the film and with chasms that are thought to have originated from shrinkage of the NiO matrix as oxygen escaped from the film. When the reduction time increased to 20 min, the pore structure becomes finer and the pore network develops further, which leads to a decrease of the surface coverage of the Ni film on the GDC/ Al_2O_3/SiO_2/Si(100) substrate. It is thought that these indicate that the reduction kinetics of Ru co-sputtered NiO films are more sluggish than that of NiO films without Ru, which is consistent with the XRD results shown in Fig. 1. The surface morphology of each film is different; which may be due to the discrepancy of the grain sizes and reduction kinetics between the deposited films. The finer pore structure of the reduced Ru co-sputtered NiO films appears to be beneficial not only to the increase of the triple phase boundary population but also to the adhesion of the films, as delamination of the film does not occur as frequently as it does in the NiO film without Ru.

To clarify the reduction kinetics of the films, an *in-situ* impedance analysis was performed on the NiO and Ru co-sputtered NiO films in 4% H_2 at 400°C while increasing the reduction time. The film was deposited on an Al_2O_3/SiO_2/Si substrate and the Au electrodes for the measurement were deposited on-plane. The measurement configuration is shown in Fig. 4. Fig. 5 shows impedance analysis results of the NiO and Ru-NiO thin films during reduction. Before the reduction started, the resistance of NiO thin film was approximately 5,500 Ω, and that of the Ru-NiO thin film was approximately 240 Ω, which is significantly lower than that of the film without Ru. This is most likely due to the higher conductivity of the ruthenium oxide compared to that of NiO.[11-13] The resistances of both films slightly increased shortly after the reduction started. It is postulated that this resulted from the fact that pores start to appear while the main matrix remains as a nonconductive phase during the initial stage of the reduction. At this stage, the reduction of NiO to Ni is insignificant and/or the amount of the conductive phase is inadequate to ensure con-
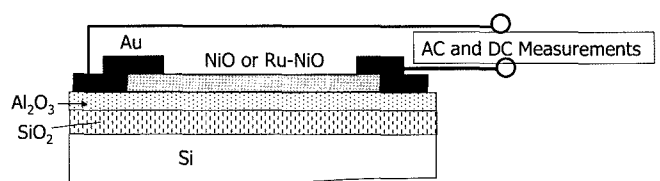

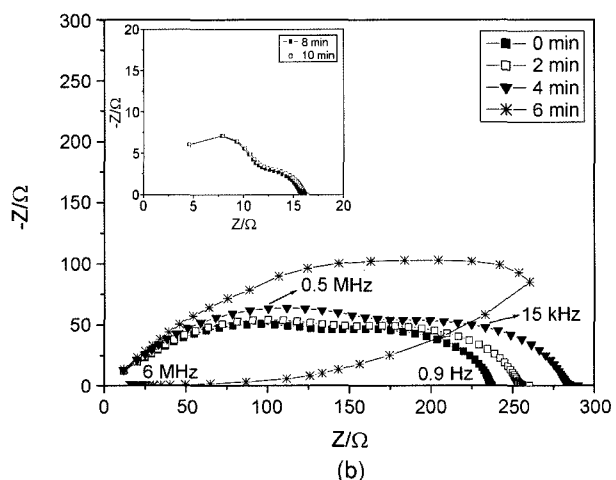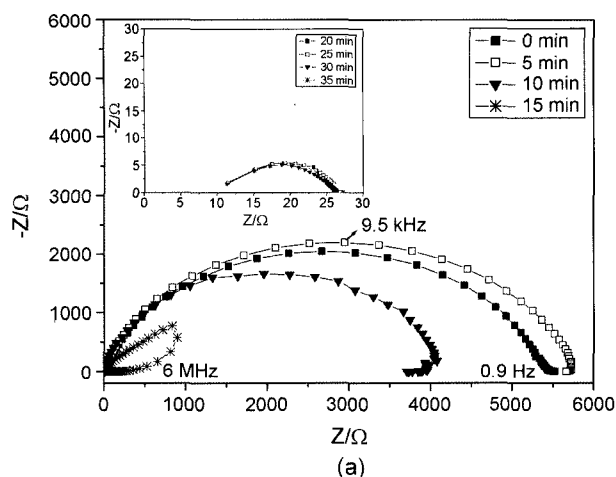**Fig. 4.** Impedance measurement configuration of the films.

Fig. 5. Impedance spectra of (a) NiO and (b) Ru-NiO thin films during reduction at 400°C in a 4% H_2 atmosphere.

Fig. 6. Resistance change of (a) NiO and (b) Ru-NiO thin films in CH_4/Air mixed gas.

nectivity in the conductor/nonconductor composite structure. Thus, it was possible to observe that the resistance of the film started to decrease as the reduction time increased. In the insets of Fig. 5, the impedance spectra after the abrupt decrease of the resistance is shown, and it is clear that the resistances of the films do not change further from a value of less than 30 Ω. This indicates that the connectivity of the conductive phases is sufficient to ensure conductance. Considering that the conductivity of the Ru-base oxide is comparable to that of the Ru metal,[10] it is postulated that the Ru-doped film could reach the percolation limit, i.e. establish a conductive network faster even if the reduction of the oxide in the matrix is sluggish.

In order to investigate the possibility of using the reduced porous film in a single chamber SOFC application, an impedance analysis was performed on porous films in a CH_4/Air ($R_{mix}=2$) mixed gas environment at 400°C. As shown in Fig. 6(a), the resistance of the Ni film increased with time in the mixed gas environment. It is hypothesized that this is evidence that part of the Ni films re-oxidizes in
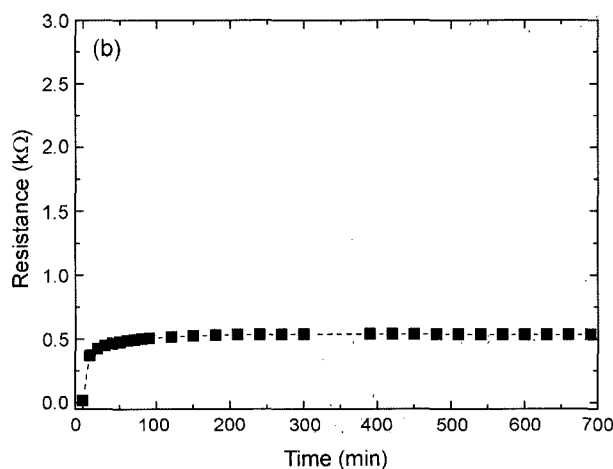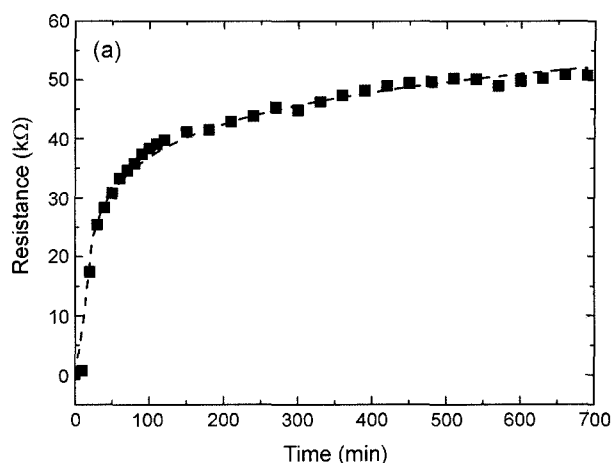
the air/fuel mixture and/or the adhesion of the film is impaired. This sudden decay of the electrical conductivity might deteriorate the overall cell performance during a single chamber operation. On the other hand, as shown in Fig. 6(b), the resistance of the Ru co-sputtered film is much less than that of the film without Ru, and its value stays lower than 550 Ω during the identical time duration in the air/fuel mixed environment. An interesting result is that the re-oxidation kinetics of the Ru co-sputtered film is much faster than that of without Ru, which is contrary to the case of reduction. Although the re-oxidation kinetics should be comprehended more clearly, the suppression of the resistance of the Ru co-sputtered NiO film in the air/fuel mixture is thought to be very impressive. From these results, the Ru addition to the Ni-base film appears to be one of the most promising methods to improve the property of the anodes of single chamber micro-SOFCs.

4. Conclusion

NiO films and Ru co-sputtered NiO films were deposited and reduced to form porous films for micro-solid oxide fuel

cell anode applications. The reduction kinetics of the Ru-doped NiO film proved to be more sluggish than that of a NiO film without Ru. The fine pore networks of the reduced Ru co-sputtered NiO film appeared to improve the adhesion of the anode film to the electrolyte layer. The possibility of using the films as anodes of single chamber micro-SOFCs was investigated through the use of an air/fuel mixed environment. It was shown that abrupt increases in the resistance are suppressed in a Ru co-sputtered film as compared to an undoped film. Hence, Ru addition to the Ni-base film appears to be beneficial to improving the stability of the anodes of single chamber micro-SOFCs.

Acknowledgment

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